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THE

AMERICAN JOURNAL OF SCIENCE.

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FOURTH SERIES.

VOL. VII—[WHOLE NUMBER, CLVII.]

No. 38.—FEBRUARY, 1899.

WITH PLATE I.

NEW HAVEN, CONNECTICUT.

1899.

TUTTLE, MOREHOUSE & TAYLOR, PRINTERS, 125 TEMPLE STREET.

Published monthly. Six dollars per year (postage prepaid). $6.40 to foreign subscribers of countries in the Postal Union. Remittances should be made either by money orders, registered letters, or bank checks.

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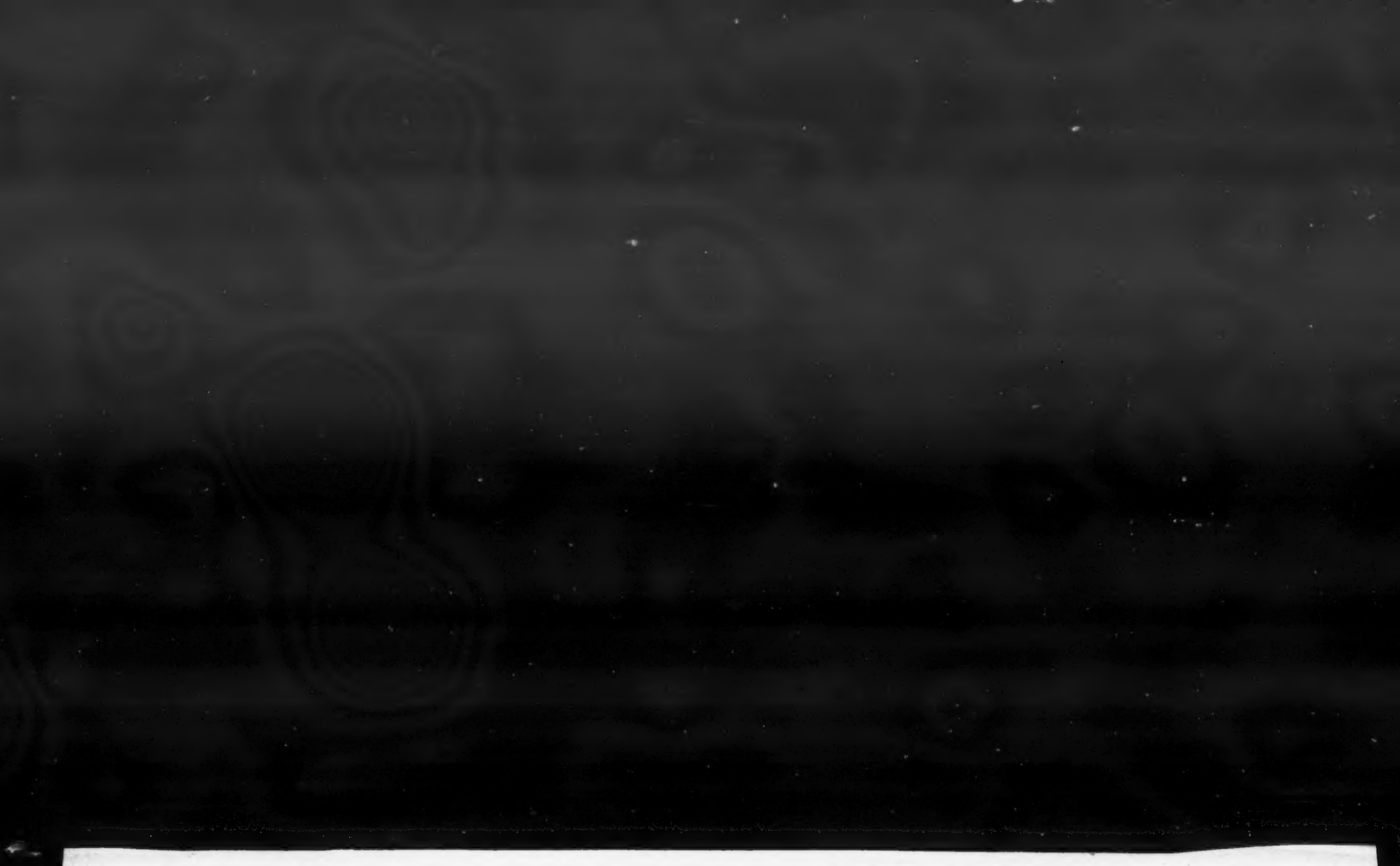

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. X.—*A Contribution to the Study of Contact Metamorphism;* by J. MORGAN CLEMENTS.

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THE various Huronian sediments which form a great portion of the iron-bearing districts of the Upper Peninsula of Michigan have in all of these districts been found to be penetrated by dikes of igneous rocks, which are predominately basic in character. The influence which these dikes exert in the formation of ore bodies where they cut the iron-bearing formations has been carefully worked out and described by Van Hise in numerous papers. The effects of contact metamorphism produced by the dikes upon the intruded sediments are of much less economic importance, and, to a very considerable extent, have been overlooked. In this paper I shall describe the products which have resulted from the intrusion of basic dikes in the Mansfield slate formation, a Lower Huronian iron-bearing formation of the Crystal Falls district of the Upper Peninsula of Michigan.*

The Mansfield formation, in its typical development, occupies a narrow valley, about three miles in length, through which flows the Michigamme River. In this valley there is situated the village of Mansfield and the mine of the same name. The formation consists of graywackes, slates (these predominate, hence the name), and phyllites, of demonstrably sedimentary origin. Associated with these, either as beds or

* For details concerning the position which the Mansfield formation holds with reference to the other Huronian rocks, the reader is referred to an article entitled The Crystal Falls Iron-bearing District of Michigan, soon to be published in the 19th Ann. Rept. U. S. Geol. Survey, and in a Monograph of the Survey.

as lenses agreeing in strike with the sedimentaries, we find slaty siderite, ferruginous chert and iron ore. The origin of the siderite and chert cannot be stated with certainty. The ore was derived from them by processes of metasomatism and concentration. All of these rocks, wherever exposed, are found to strike north and south, with at times slight variations from this direction, probably due to minor crumpling of the formation. The dip is high to the west at about 80°.

Overlying the Mansfield slates is the volcanic Hemlock formation.

Immediately east of the slates, that is, stratigraphically under them, there occur continuous masses of coarse dolerite (diabase), which cut off the slates in their strike, both to the north and to the south. No well-characterized dikes of dolerite cutting the Mansfield formation have thus far been found, either by surface studies or by underground exploration. In no instance, moreover, has a direct contact between the dolerites and the slate formation been observed, owing to the contacts being covered by disintegration products, although in many instances these rocks are separated from each other by spaces only a few feet in width. That the relations between the two, however, are those of igneous intrusion, is shown by the fact that the dolerites cut across the strike of the slates. Furthermore, if we make a traverse from the dolerites westward into the slates we notice the following. On the westward flank of the dolerite ridge we find associated with the dolerites masses of hard, peculiar, hornstone-like rocks, which have a well-banded character and in places are of large size and very numerous. Leaving this zone we reach the valley proper, in which lie the normal sedimentaries of the Mansfield formation. It thus appears that we have an intermediate zone between the dolerites and the slates. The banded rocks forming, with the associated dolerites, this intermediate zone, are believed to be sedimentary rocks which have been metamorphosed by the dolerites.

The exact original characters of these sedimentary rocks cannot be stated with positiveness. They are believed to have been slates having essentially the same general physical characters and mineral and chemical composition as the slates which now lie next to the contact zone and extend away from it for several hundred feet across the strike, without showing any noticeable changes in character. Although original chemical variations exist in these slates, as is shown by the banding, and did exist in the slates from which the metamorphosed products to be described were derived, as is shown by the banding in them,—nevertheless, such initial variations in these rocks is of a quantitative rather than qualitative character, and it is not

believed that they can vitiate the conclusion concerning the effect of the metamorphic action upon the slates.

In the further discussion, therefore, it is assumed that the noteworthy differences between the rocks to be described are due to metamorphic action, and are not due to the original chemical differences. This assumption seems to be warranted by the fact that the changes are in perfect accord with those described from similar dolerite-slate contact zones in other areas.

The products of the contact metamorphism are those banded and spotted rocks which have been called spilosites, desmosites, and adinoles, and they will be the special subject of this article.

The dolerites (diabases) are coarse-grained, and do not exhibit anything of especial interest, consequently no description will be given of them. No evidence of any endomorphic action whatever has been observed in them.

In a study of contact action it is, of course, of the greatest importance to be able to determine accurately the order of succession from the unmetamorphosed to the most metamorphosed forms of the rocks. In the present case it is impossible to compare sections from, or analyses of, any given stratum of the rock at successive stages of approach to the line of contact, for the reason that, where the exposures were found, the dolerite had been intruded parallel to the strike of the slates. Moreover, the exposures are very poor, indeed. This order of succession has, however, been made out so satisfactorily for other localities by Lossen and others, and the characters of each rock in the succession have been so well described, that I have no hesitation, after microscopical study of thin sections of the specimens, in presenting the series in the following order. Beginning with the clay-slate, the least metamorphosed rock in the district, and the ones farthest removed from the intrusives, we pass to the phyllites, then to the spilosites and desmosites, and finally to those which are known as adinoles, the latter being those which occur next to the intrusive.

The Clay-slates.

These are dull and lusterless banded rocks, ranging in color from black to olive-green and red. They are usually impregnated with more or less iron pyrites in large macroscopical crystals. By high power, one can very readily distinguish in the slates round or oval areas of limpid quartz, surrounded by a dark grayish mass, which consists of minute flakes of white mica, crystals of rutile, and some of hematite, here and there a long, transversely-fractured, greenish needle, taken for actinolite, and, lastly, a dark grayish to black granular aggregate, which is the chief coloring matter of the slate, and which makes up a very considerable part of the rock. This aggre-

gate is presumed to be of clastic origin, and to be chiefly feldspathic dust, darkened by carbonaceous and ferruginous specks. Careful search was made for flakes of chlorite and biotite, but no traces of either mineral could be found. Likewise, feldspar is absent in grains or crystals of a size which could be recognized. The banding of the slates is occasioned by the varying quantities of these minerals, although each band contains some individuals of all the kinds enumerated. All the crystals lie with their long axes parallel, causing the cleavage of the slate. It is clear that the slate is already in what we may perhaps call a semicrystalline state, the crystals of white mica, actinolite and rutile evidently being new developments in the sediments.

Origin and composition of the clay-slates.—The origin of the clay-slates of the Mansfield formation is probably to be looked for in the disintegration and decay of the Archæan granite and the subsequent compression of the resulting clay; for between the Archæan granites and the Mansfield slates no other rock masses are known to have existed in this region from which the clay could have been derived.

An examination of series of analyses of granites shows that while the relative percentages of soda and potash vary considerably, on the whole the potash is the higher of the two. As a consequence of the easier solubility of the soda, this relation between the alkalies, soda and potash, is maintained, and is often very striking in clay-slates. An average of thirty-one analyses of clay-slates taken from various sources shows two and one-half times as much potash as soda. In the case of the Mansfield slate, it will be seen that the difference is much greater, there being present ten times as much potash as soda.

ANALYSIS OF MANSFIELD SLATE.

(By Mr. Geo. Steiger, U. S. G. S.)

SiO_2	60·28
TiO_2	·69
Al_2O_3	22·61
Fe_2O_3	2·53
FeO	·45
MnO	trace
CaO	·13
BaO	·04
MgO	1·35
K_2O	5·73
Na_2O	·54
H_2O at 100—	·60
H_2O at 100+	3·62
P_2O_5	·03
CO_2	none
C	·97
Total	99·57

The relative proportion of the alkaline earths, lime and magnesia, is also striking, the latter being present in the greater quantity. As a general rule, in igneous rocks (and to igneous rocks all clay-slates owe their ultimate origin) the reverse condition exists, i. e., the magnesia is subordinate in quantity to the lime, except in the ultra basic non-feldspathic kinds. The carbon present in this slate is considered as offering trustworthy evidence of the presence of organic life at the time of the deposit of the slates, though no more satisfactory evidence of the existence of life thus early has ever been found. It will be noticed finally that considerable water is present, but in consideration of the character of the rock this is to be expected, and if anything the value is low. These clay-slates are the rocks which are nearest the original sediments.

Phyllites.

The phyllites have a silky luster and bluish black color. They are composed essentially of white mica, which occurs in large quantity surrounding grains of quartz and feldspar (?). Rutile occurs in single crystals and in clumps of small crystals scattered through the mica. Associated with it, there occur here and there flakes of hematite, and small aggregates of black, undeterminable specks. Apparently, no interstitial material, such as occurs in the clay slates, is here present.

These rocks seem to differ from the clay slates only in that they are more completely crystalline, the interstitial material of the slates having disappeared. Owing to the apparently unimportant differences which exist between the clay-slates and the phyllites, no analyses have been obtained of the latter.

Spilosites, Desmosites, and Adinoles.

With these rocks we begin the consideration of the true contact products of the dolerite. These contact rocks possess certain characters in common. They are dense, flinty, "hornstone-like" rocks, which in some cases still show the fine banding of the original slates. Others are very characteristically spotted. They have a splintery, and at times almost conchoidal fracture, and vary in color on fresh fracture from light to very dark gray and greenish. The weathered surface, in almost all cases, is covered by a thin, white to light yellowish crust. The mineralogical components are quartz, feldspar (albite), biotite, chlorite, white mica, actinolite, rutile, epidote,

and iron oxide. Various combinations of these minerals occur, and likewise the textures vary. As a result of these variations there are produced the different kinds of contact products known as spilosites, desmosites, and adinoles. The characters of the minerals showing nothing unusual, I shall briefly describe the textures and mineral combinations which characterize these various rocks.

Spilosites—The ordinary spilosites are distinctly mottled in the hand specimen, and show clearly to the naked eye in thin section the oval spots which characterize them. These oval areas are very commonly four millimeters long, and in rare cases even longer. They are frequently connected, forming chains. The spots are very appreciably darker than the mass in which they lie, and are composed of aggregates of chlorite, quartz, feldspar, and rutile, with a small amount of white mica. The chlorite is the chief constituent of the spots and gives them their dark color. The surrounding mass consists essentially of white mica, quartz and feldspar, small epidote and rutile crystals, flakes of hematite, and with a very slight amount of chlorite. The different proportions of chlorite and muscovite cause the difference between the spots and the groundmass. In some of the spilosites we find a few flakes of biotite and needles of actinolite. However, these are always very subordinate in quantity to the chlorite.

Other spilosites have been noted in this area in which the spots are white and lie in a fine-grained dark mass composing the greater part of the slides. So far as I can learn, only one similar instance of the occurrence of such a variety of spilosite has been described. This is by Van Werveke, to whose description reference is made by Zirkel* and Rosenbusch.†

The white spots are composed essentially of feldspar, with only a minor amount of chlorite and epidote. The feldspar grains are much larger than those which take part in the constitution of the mass surrounding the spots. This surrounding mass is made up of quartz, feldspar, chlorite, epidote, some sphene, with sheaves of actinolite scattered through it. In one section flakes of biotite were observed mixed with the chlorite, though in very subordinate quantity.

* Zirkel. Lehrbuch der Petrographie, 2d edition, vol. ii, 1894, p. 719.
† Rosenbusch. Mikroskopische Physiographie, 3d edition, vol. ii, 1896, p. 1127.

ANALYSIS OF SPILOSITES.

	1.	2.
SiO_2	52·51	57·77
TiO_2	1·70	·92
Al_2O_3	19·00	19·35
Cr_2O_3	none	none
Fe_2O_3	3·31	1·29
FeO	7·19	3·37
MnO	trace	trace
CaO	1·55	1·71
BaO	trace	none
SrO	trace	trace
MgO	3·29	4·35
K_2O	·70	·22
Na_2O	6·72	8·22
Li_2O	trace	none
H_2O at 110°	·34	·18
H_2O above 110°	3·26	2·34
P_2O_5	·15	·04
CO_2	none	none
S and SO_3	none	none
C*		
Cl	none	none
F	trace	none
Total	99·72	99·76

No. 1, Spilosite, Spec. 32861 Lake Superior Division U. S. Geol. Survey, from Mansfield, Michigan, Dr. H. N. Stokes, analyst.

No. 2, Spilosite, Spec. 32827 Lake Superior Division U. S. Geol. Survey, from Mansfield, Michigan, Dr. H. N. Stokes, analyst.

Desmosites.—Under the desmosites are included contact products composed of the same mineral constituents as the spilosites, but which instead of being spotted show a distinctly banded structure. That these are very closely related to the spilosites, and that in fact they grade into each other is shown by the study of one rock. A section from this, examined under the microscope, shows irregularly rounded areas which consist of ragged bunches of chlorite and aggregates of rutile and epidote, with some flakes of biotite lying in a quartz-feldspar mass. As these spots increase in number they approach each other and unite, forming streamers which in their turn unite and form bands. No analysis has been obtained of the desmosites, as it was so evident that they contain nothing different from the spilosites.

Adinoles.—Thus far chlorite has been the chief dark constituent of the contact products mentioned, whereas actinolite is

* C was not determined.

either totally absent or else is present merely as an accessory. In the adinoles actinolite is the characteristic constituent. The minor constituents, as a rule, are more uniformly distributed than in the spilosites. However some spots are present and are composed essentially of actinolite. The actinolite is present in sheaf-like growths, lying commonly in an exceedingly fine-grained mass of quartz and albite, with some flakes of chlorite and grains of epidote. The adinole is rendered rather dark by minute black specks which are disseminated through it. In places these are collected in irregular or lenticular heaps. They seem to be carbonaceous matter.

ANALYSIS OF ADINOLE FROM MANSFIELD, MICHIGAN.

(By Mr. Geo. Steiger, U. S. G. S.)

SiO_2	74·16
TiO_2	·37
Al_2O_3	11·85
Fe_2O_3	·82
FeO	1·66
MnO	·06
CaO	2·10
BaO	none
MgO	2·10
K_2O	·15
Na_2O	6·57
H_2O at 100°−	·05
H_2O at 100°+	·52
P_2O_5	·08
CO_2	·09
C	·18
Total	100·76

Other varieties of the contact rocks.—There is still another kind of contact rock in which actinolite is the chief dark constituent, and in this the actinolite is mainly collected in bands. This rock thus corresponds to the desmosites (banded chlorite rocks) in structure, though differing from them in mineralogical composition.

The chlorite and actinolite contact rocks may be expected to grade into each other, and such a gradation is shown in one specimen, in which actinolite and chlorite are present in about equal quantity. The actinolite occurs in crystals and sheaves, forming spots; whereas the main mass of the thin section surrounding the spots is formed by chlorite as the dark silicate, associated with feldspar, quartz, and some epidote.

Comparison of analyses.—From previous determinations in other regions it is well known that the adinoles are next to the

contact, while the spilosites (and desmosites) are intermediate between them and the clay-slates. The following series of analyses are arranged in the order of approach to the dolerite, as determined by the character of the rocks:

	1.	2.	3.	4.
SiO_2	60·28	52·51	57·77	74·16
TiO_2	·69	1·70	·92	·37
Al_2O_3	22·61	19·00	19·35	11·85
Cr_2O_3		none	none	
Fe_2O_3	2·53	3·31	1·29	·82
FeO	·45	7·19	3·37	1·66
MnO	trace	trace	trace	·06
CaO	·13	1·55	1·71	2·10
BaO	·04	trace	none	none
SrO		trace	trace	
MgO	1·35	3·29	4·35	2·10
K_2O	5·73	·70	·22	·15
Na_2O	·54	6·72	8·22	6·57
Li_2O		trace	none	
H_2O at 100° −	·60	* ·34	* ·18	·05
H_2O at 100° +	3·62	† 3·26	† 2·34	·52
P_2O_5	·03	·15	·04	·08
CO_2	none	none	none	·09
S and SO_3		none	none	
C	·97			·18
Cl		none	none	
F		trace	none	
Total	99 57	99·72	99·76	100·76

No. 1, Clay-slate, Spec. No. 32497 L. S. D., U. S. G. S. Analyst Mr. Geo. Steiger.

No. 2, Spilosite, Spec. No. 32861 L. S. D., U. S. G. S. Analyst Dr. H. N. Stokes.

No. 3, Spilosite, Spec. No. 32827 L. S. D., U. S. G. S. Analyst Dr. H. N. Stokes.

No. 4, Adinole, Spec. No. 32465 L. S. D., U. S. G. S. Analyst Mr. Geo. Steiger.

In these analyses the usual increase of silica as the dolerite is approached is at once noticeable, and hand in hand with it goes the diminution in percentage of alumina and iron oxides. The content of water and carbonaceous‡ matter also suffers diminution, as was to be expected.

The most noteworthy difference between the clay-slate and the contact rocks is shown in the relations of potash and soda. This is well brought out in an examination of analyses Nos. 1

* H_2O at 110°. † H_2O above 110°.

‡ The C in Nos. 2 and 3 was not determined.

and 2. It will be seen that there is only about $\frac{1}{8}$th as much potash in the contact rocks as in the normal clay slate; while, on the contrary, about 12 times as much soda as there was in the slate has been added to the contact rock. This causes a reversal of the relations of the soda and potash, so that, whereas in the clay-slate there is present 10 times as much potash as soda, we find in the contact rock taken as an example very nearly 10 times as much soda as potash.

Comparison of Mineralogical Composition.

It will be sufficient for our present purpose to consider the clay-slate, on the one hand, and the spilosite and adinole on the other. To recapitulate briefly, in the clay-slate we have quartz (clastic), white mica, actinolite, rutile, and an indeterminate interstitial material of finely granular character, discolored by carbonaceous and ferruginous matter. This interstitial material we may consider as that remnant of the original feldspar, quartz, biotite, and iron ore dust in the original clay which was not used in the production of the white mica, actinolite, and rutile now found in the clay-slate. Original chemical differences in the slate are shown by the arrangement of the various materials in bands, certain bands containing a greater quantity of white mica; hence, the conclusion that these were probably richer in alkali than the adjoining bands, which are poor in white mica.

In the spilosite and adinole we find present quartz—but not clastic—white mica, actinolite, and rutile, as in the clay-slate. But in addition there is albite, chlorite, epidote, and biotite. There is nothing in these rocks which shows clastic origin. The original sediment has been completely recrystallized and there remains only the banding to point to the sedimentary origin of the rock. The clastic quartz has been destroyed by solution or aqueous fusion, and has been recrystallized, and now forms a mosaic with the albite. Albite, for whose production some of the silica of the clastic quartz may have been used, is present in the rock in considerable quantity, in contradistinction to its total absence from the slate. The initial quantitative chemical differences existing in the clastic rock are also shown in the recrystallized rock by differences in the mineralogical composition, a large quantity of chlorite, for instance, forming a band adjacent to a band poor in chlorite, thus indicating a richness of the first band in magnesium. The greatest difference existing between the practically unmetamorphosed slate and the contact product is the evidence in this last of complete recrystallization, and the presence of albite in large quantity.

Cause of Chemical and Mineralogical Changes in the Rocks described.

The changes which have taken place in sedimentary rocks as the result of contact with igneous rocks have given rise to a great deal of discussion. The one school, notably represented by the French geologists, contends that there is an actual transfer of material from the igneous rock to the rock intruded with more or less complete resorption of the latter; whereas the other school has maintained that the indisputable metamorphism observed in such cases is due chiefly to the action of the so-called mineralizers. Studies upon a series of contact rocks similar to those here presented have given foundation for the view upheld by Roth,* Zirkel,† and others, that in the case of contact metamorphism produced by basic rocks an actual transference takes place. This view has been recently very strongly advocated by W. Maynard Hutchings,‡ who has described some interesting products, which result from the contact of the Whin Sill, which still further support it.

The very considerable changes which are shown by the above analyses to have taken place in the metamorphism of the slates, especially the change in the amount of silica and soda resulting in the production of albite in large quantity, seem to add weight to the supposition that in such contacts an actual transfer of material, possibly in the form, as has been suggested by others, of a soda silicate, does take place from the basic igneous rock to the intruded slate.

MADISON, WIS.

* Chemische Geologie, by J. Roth: Berlin, 1890, vol. iii, p 145.

† Lehrbuch der Petrographie, by F. Zirkel: Leipzig, 2d edit, vol. ii, 1894, p. 722.

‡ Notes on the composition of clay-slates, etc., and on some points in their contact metamorphism, by W. M. Hutchings: Geol. Magazine, vol. i, dec. 4, 1894, p. 75.

An interesting contact rock, with notes on contact metamorphism, by W. M. Hutchings: Geol. Mag, vol. ii, dec. 4, 1895, p. 122-131, 163-169.

ART. XI. — *The Origin of Mammals;** by HENRY F. OSBORN.

SINCE the source of the Mammalian phylum was later than that of the Reptilian phylum in the Permian and possibly Carboniferous, we are sure that it extended at least very far back into the Triassic, and the Triassic was apparently a time of great continental connections and of consequent wide geographical distribution even of land types.

In presenting a phylogenetic chart which traces the ancestry of Mammals to the Upper Permian, I am quite as conscious as the most conservative zoologist present that we are not on sure ground, that this is a castle of cards liable to fall at any moment. Yet such a chart, involving as it does numberless hypotheses, is necessary to set forth certain ideas.

Clearing the way for this discussion, this chart first replaces the general view defended by Huxley in 1880, of a genetic succession between three sub-classes of mammals, which has become a matter of creed with many zoologists. In the last eighteen years not a scintilla of evidence has arisen to show that Placentals are descended from Marsupials, and of late, evidence has been coming in directly against this view. In fact zoo-palæontology now indicates that Marsupials and Placentals are parallel phyla, arising from a common stock, while Monotremes are so different that they may even be considered diphyletic, or derived independently from the Reptilia, as maintained by Mivart among others, and latterly by Seeley.

So far as major classification is affected by this conception, it appears therefore that we must revert to Gill's divisions of 1872, constituting only two sub-classes of Mammals, namely:

A—*Eutheria*	and B—*Prototheria.*
Marsupials, Placentals.	Monotremes.

Marsupials are less primitive than the placental Insectivores, and Marsupials and Placentals are certainly far nearer each other than either are to the Monotremes.

To guide our speculation in the unknown pre-Tertiary period, we may gather certain positive principles from the known evolution of the Tertiary mammalia. First, we know that *adaptive radiation*, characteristic of all vertebrates, and beautifully illustrated among Reptilia, is in a very high degree distinctive of Mammalia, because of their superior plasticity.†

*Opening the discussion before the International Congress of Zoologists at Cambridge. (In conjunction with Professor H. G Seeley.)

† We know nothing of Africa, whether it enjoyed a radiation of its own or borrowed its fauna from other continents.

There is the (I) *Marsupial radiation of Australia* (Meteutheria)*—now passing its prime, then the (II) *Tertiary Placental radiation of the Northern Hemisphere* (Ceneutheria), and another quite independent (III) *Tertiary placental radiation in South America*, (rendered less pure in course of the Tertiary period by migration from I and II). IV, There is the entirely distinct and archæic *Cretaceous Placental Radiation of the Northern Hemisphere* (Meseutheria), which extends into the Tertiary, and may have given origin to II and III, although as yet we have no direct proof of it.

We mark the fact that the above radiations are all of *ordinal* rank, for the Marsupial radii, although termed families, are adaptively equivalent to several Placental orders.

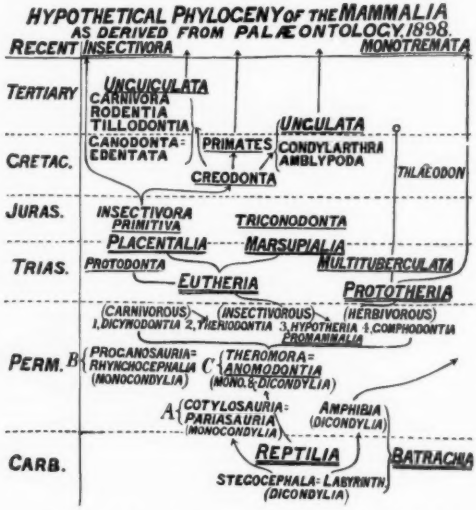
If we apply these same principles to the Jurassic, we apparently have evidence of a more fundamental (V), *Sub-class radiation of Placentals and Marsupials, and probably Monotremes*, of world-wide distribution. (This involves a controverted question, to which I shall revert, for by some zoologists these animals of the Purbeck Clays, Como Beds, and Stonesfield Slates are considered exclusively Marsupials and Monotremes.) Finally far back in the Perm-Trias we certainly observe (VI), the *Theromorph or Theriodont Reptilian radiation*, spurs of which may have given rise to the Mammalia.

The *focal-types*, or most primitive forms of the radiations, I—IV, *were certainly small, terrestrial, clawed, insectivorous or omnivorous forms.* It is noteworthy that in the evolution of each radiation, so far as we know at present, land types and organs are invariably primitive, and water types and organs are secondary, exactly as we find it among the Reptilia. In fact we have not found a single instance in which a mammal or reptile series is known to be transforming from a water into a land type; it is always the reverse. There is certainly no evidence for a cetoid (Albrecht) stem of the Mammals. Again it is obvious that neither carnivorous nor herbivorous types with highly specialized or reduced teeth and feet can be so central as insectivorous and omnivorous types. In fact the Insectivores among Placentals, and Opossums among Marsupials, are the only animals which have preserved the dental prototype close to that of the Promammal.

The backward convergence of all Tertiary mammalia to a Creodont stem, as indicated in the chart, affords the clearest demonstration of the existence of an earlier insectivorous stem, and it not only accords with the above principles, but we are thus carried a step further to realize that the Creodont ancestor must have been a generalized Insectivore.

* The Eutheria may embrace the Meteutheria or Marsupials, the Meseutheria or primitive Mesozoic Placentals, the Ceneutheria or Tertiary Placentals.

To reconstruct the ancestral Eutherian skeleton, therefore, we should divest the Creodonta and Insectivora, in their anatomy and development, of all their secondary specializations, and combine all their truly primitive characters. This ideal Eutherian is nearer the pro-Marsupial than we supposed: it has the following chief characters: Head large, body relatively small. Anterior nares terminal, face elongate. Insectivorous or omnivorous habit. Molar teeth pointed, tritubercular. Typical dental succession. Vertebræ with intercentra. Dorso-lumbars not exceeding 20. Back arched, tail long and powerful. Scapula and ilium narrow, acuminate. Humerus with powerful



deltoid crest, condylar crests and entepicondylar foramen. Femur with three trochanters. Feet plantigrade. Centralia and tibiale. Fore-limb more or less prehensile, elbows everted.

Now the Creodonta are members of that Cretaceous radiation, IV, which we find in full bloom in the Basal Eocene, mingled with the dying group of Multituberculates, which belong to the Jurassic radiation, V.

In the Mid—and Uppermost Jurassic (Stonesfield, Purbeck and Como Beds) however, occur all three types, which theoretically constitute radiation V: first, the *Triconodonts* primitively but typically *Marsupial* in structure; second, the *Insectivora primitiva*, primitively *Placental* in type, insectivorous and without a single Marsupial character either in jaw or teeth; third, the *Multituberculata*, whose sub-class position is now assumed to be *Monotreme*.

Always keeping in mind that our direct evidence here is of the most limited character, since we have neither skulls nor skeletons, only teeth and jaws, we are tempted to hypothetically connect the Creodonta with the Insectivora Primitiva, and to assume that there existed in the Mid-Jurassic, as above stated, the well advanced radiation V of the two sub-classes of EUTHERIA and PROTOTHERIA as defined by Gill.

The problem of the Origin of the Mammals now resolves itself into the connections between these two sub-classes either with the Reptilia or Amphibia, and we turn back to the three contemporary Upper Permian reptile groups:

1. *Pareiasauria or Cotylosauria*, land animals with a solid skull and replete with Stegocephalian or Amphibian characters, certainly the most primitive reptiles.
2. *Proterosauria or Proganosauria*, with an open two-arched skull, specialized reptiles, which have apparent affinities with the Crocodilia, Dinosauria, Rhyncocephalia and Squamata (Dolichosauria, Mosasauria, Lacertilia and Ophidia).
3. *Theriodontia or Theromora* (*Dicynodontia, Cynodontia and Gomphodontia*), with an open, single-arched, skull (as in the Chelonia, Plesiosauria, Icthyosauria and Mammalia).

The Theriodontia as perceived by Owen in 1876, and now fully confirmed by Seeley, are astoundingly mammalian in type. They are essentially quadrupedal, long-limbed, terrestrial reptiles, totally dissimilar from all other reptiles, and standing far away from them. They also present an advanced stage of functional radiation in tooth and skull structure in adaptation to carnivorous, omnivorous and herbivorous habits, to which, when known, their skeletons will probably be found to conform. The shoulder girdle is of Monotreme type; in other features of the skeleton they are strikingly like the ancestral Eutherian, described above. The skull may in fact be reduced to the Eutherian type by the coalescence of the prefrontals, postorbito-frontals and quadrates with the adjacent elements, and by the loss of the ectopterygoids or transverse bones. The teeth are promammalian in formula, and pro-tritubercular or multitubercular in form. The skeleton so far as known is partly Eutherian, partly Monotreme or Prototherian.

Two alternatives at this point present themselves: First: Are the Monotremes directly derived from such a type as these Theriodonts, leaving an independent derivation for the Eutherian or Marsupio-placental stock, as has been suggested by Seeley? Second: Must we set aside the Theriodonts for an Amphibian stem form on account of the numerous Amphibian resemblances which Hubrecht and others find in the development and anatomy of the lower Mammalia?

The first question is now unanswerable, although at present the evidence that the Mammalia are diphyletic is certainly considerable. Second, the investigation of the placental ovum rises to extreme importance; if the Eutherian ovum is of Amphibian type, the Mammalia are certainly diphyletic, for the Monotreme ovum is certainly of reptilian type. This point may be met by supposing that at the time the Marsupio-placentals were given off, the Theriodontia conserved a number of Amphibian characters, which were at the time or subsequently lost.

The problem of most immediate concern, therefore, is whether the Theriodontia are actually the long-sought Promammalia of Hæckel, Hypotheria of Huxley or Sauromammalia of Baur, or whether they present a fresh instance of extensive parallelism due to the assumption of habits analogous to those of Mammalia. Professor Seeley has just presented the latter view,* and it is certainly true that none of the known Theriodontia fill the characters outlined above as those we must look for in the Promammal or Eutherian stem, for they are all too large and too specialized.

There are however grounds for the more sanguine former view, that the Theriodontia are the Hypotheria or Promammalia, because it appears that *within the order may well have existed some small insectivorous types, far less specialized in tooth structure than either the carnivorous Cynodonts or herbivorous Gomphodonts, as one of those conservative spurs of adaptive radiation which form the focus of a new progressive type.*

The problem will therefore be settled by additional discovery and knowledge of the structure of the diverse types which undoubtedly composed this remarkable group.

NOTE. We can happily preserve that part of Huxley's speculation upon the origin of the Mammals which pictured the Insectivora as nearest the ancestral type. The Amphibian (or Stegocephalian) origin of the Mammalia which he defended, is wholly set aside, if the view here taken is correct, for the Theriodontia are certainly not Amphibia in any sense.

* "Anomodonts are not the parents of Mammals, but a collateral and closely related group. The common parent of both may be sought in rocks older than Permian, perhaps in Silurian or Devonian strata." Printed abstract of Professor Seeley's argument, p. 3.

Art. XII.—*On the Chemical Composition of Tourmaline;* by S. L. Penfield and H. W. Foote.

Introduction and Historical.—There is probably no common mineral whose chemical composition has proved more perplexing and been so little understood as tourmaline. Some reasons for this are, first, that the mineral presents certain peculiarities in chemical composition of an unusual nature; second, the analysis of tourmaline has been one of the difficult problems of analytical chemistry, hence reliable data for the calculation of the formula have not been easily obtained; and, lastly, although good analyses have been made, the results have not been thoroughly relied upon, nor have they been interpreted to the best advantage. The present investigation was undertaken, therefore, with the hope that by making a few analyses with the utmost possible care on tourmalines of exceptional purity, it would be possible to find a satisfactory explanation of the chemical composition of this interesting mineral.

In order to appreciate the problem in hand, it will be necessary to review briefly the work and the results of previous investigators.

The analyses of Vauquelin and Klaproth, made in the early part of this century, were naturally defective, because at the time they were made, lithium was unknown, it had not been discovered that tourmaline contained boron, and analytical methods were not perfected.

In 1818 the presence of boron was detected by Lampardius,* and in the same year Arfvedson† discovered the new alkali metal lithium, and showed its presence in spodumene, petalite and tourmaline.

In 1827 Gmelin‡ published analyses of ten varieties of tourmaline, but his results led to no satisfactory formula, although the essential constituents of the mineral, with the exception of the boric oxide, were determined with a considerable degree of accuracy.

In 1845 Hermann§ published the results of four analyses of tourmaline from Russian localities. He proved conclusively that the iron was ferrous, and not ferric as considered by previous investigators. Boric oxide was not directly determined, but estimated by difference, and the results compare favorably with the direct determinations made by our present methods.

* Ann. d. Phys. u. Chem., xxx, p. 107.
† Schweiger's Jour. d. Chem. u. Phys., xxii, p. 111.
‡ Pogg. Ann., ix, p. 127.
§ Journal für prakt. Chem., xxxv, p. 232.

He was the first to point out that silica and boric oxide are present in the definite molecular proportion 4 : 1. He erroneously decided that tourmaline contained carbon dioxide, the reasons being as follows: It was generally believed at that time that the mineral contained no water, as stated by Hermann "*die Turmaline keine Spur davon enthalten*," and it is true that when fragments are tested by the usual method of heating to redness in a closed tube no water is obtained. It is only when the material is heated *intensely*, best as fine powder, that hydroxyl is decomposed and water given off. When Hermann dissolved fragments in a borax bead he observed that a gas was evolved, and, since it was believed that this could not be water vapor, he supposed that it must be carbon dioxide. Pains were taken to fuse some of the mineral in a tube with borax, and to conduct the gas into lime water, by which treatment a precipitate was obtained which effervesced with acids, but it is safe to assume that the carbon dioxide thus detected was derived from improperly purified air and not from the mineral.

In 1850 Rammelsberg* published the results of the analyses of thirty varieties of tourmaline. The execution of such a large number of analyses must be regarded as a very great undertaking, since at that time gas and many facilities of our modern laboratories were not available, and many methods of analysis were not perfected. Special evidence is given that great care was taken in the selection of material for analysis and in the analytical methods, which appear to have been well chosen and reliable in character. The analyses, however, were defective in several important particulars. Thus the iron was regarded chiefly as ferric. Believing, like Hermann, that tourmaline contained no water, and having detected the presence of fluorine in some varieties of the mineral, he supposed that the considerable loss on ignition which occurred was due to the volatilization of silicon fluoride, and from this loss he estimated fluorine to be present in amounts varying from 1·30 to 2·51 per cent. Direct determinations of boric oxide were made in three cases only, and in the remaining analyses this important constituent was estimated by difference. Although the analyses led to no satisfactory formula, they indicated certain prominent characteristics of the mineral, namely, the great variation in the relative amounts of aluminium, iron, magnesium and alkalies, and the nearly uniform amounts of silica and boric oxide.

Fully realizing certain defects in his earlier analyses, Rammelsberg† published in 1870 a revision of his former paper.

* Ann. der Phys. u. Chem , lxxx, p. 449 and lxxxi, p. 1.
† Ann. der Phys. u. Chem., ccxv, pp. 379 and 547.

At this time it was shown that all varieties of tourmaline contained chemically combined water, and the amount of water was estimated from the earlier determinations of the loss on ignition after making certain corrections for volatilization of silicon fluoride. He found that the iron was chiefly if not wholly ferrous, and recalculated accordingly his earlier results. Six direct determinations of boric oxide were made, and it is pointed out that these amounts correspond closely with the indirect determinations by difference. As a result of the revision, Rammelsberg reached the conclusion that all tourmalines are derived from the acid H_6SiO_5. In this he considered the hydrogen atoms to be replaced by metals of different valences, or, in other words, he regarded tourmaline as composed of a mixture of the following molecules:

R'_6SiO_5	R' = Na, K, Li and H.
R''_3SiO_5	R'' = Fe, Mg, Mn and Ca.
R'''_2SiO_5	R''' = Al and B.

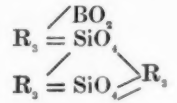
Furthermore he decided that certain varieties correspond closely to the special formulas

$$\text{I.} \begin{cases} R'_3Al_2BSi_2O_{10} \\ R''_3Al_4B_2Si_4O_{20} \end{cases} \quad \text{and} \quad \text{II.} \begin{cases} R'_6Al_{12}B_4Si_9O_{45} \\ R''_3Al_{12}B_4Si_9O_{45} \end{cases}$$

while he regarded others as mixtures of these two molecules. By substituting hydrogen atoms for the metals and boron of these special formulas, the acids become respectively $H_{24}Si_4O_{20}$ and $H_{54}Si_9O_{45}$, both of which are multiples of H_6SiO_5. He concluded that the SiO_2 and B_2O_3 are not present in a definite molecular proportion, but that boron plays the part of a metal and is isomorphous with aluminium.

In 1888 Riggs* published the results of twenty analyses of various types of tourmaline from American localities. The analyses were executed in the laboratory of the U. S. Geological Survey at Washington, and bear every evidence of being made with the precision and care characteristic of the analytical work of that laboratory. Boric oxide, water and ferrous oxide were determined directly by reliable methods, and a high degree of accuracy is claimed for the analyses. A careful description of the quality of the material analyzed is not given, and although it is to be supposed that great care was taken in its selection, the following statement has left this in doubt: "The analyses do not represent ideal compounds, but are made of material more or less impure . . . . " Riggs concludes that the analyses give "as a general tourmaline formula the simple boro-orthosilicate $R_9BO_3 2SiO_4$" which is expressed graphically as follows:

*This Journal, III, xxxv, p. 35.



He supposes R to include H, Li, Na, K, Ca, Mg, Fe, Al and small amounts of the Al–O or possibly Al-OH radicals. It may here be stated that the foregoing formula is identical in type with the special formula $R'_3Al_2BSi_2O_{10}$ ($H_9BSi_2O_{10}$) of Rammelsberg, and considering boron as replacing hydrogen like a metal the silicic acid from which the formula is derived becomes $H_{12}Si_2O_{10}$ or H_6SiO_5. Riggs further states that, owing to slight variations, the ratios give nearly the "equally simple general formula $R_{10}BO_2 2SiO_4$," stating that "between these two views there are at present no means at hand of deciding." It would seem, however, that the last formula is impossible, for, considering hydrogen atoms as replacing R_{10}, the acid can not be split up like other oxygen acids into silicic and boracic anhydrides and water. There are also given the following special formulas for three pronounced types of tourmaline:

I. Lithia tour.	$12SiO_2$, $3B_2O_3$, $4H_2O$, $8Al_2O_3$, $2(NaLi)_2O$.
II. Iron tour.	$12SiO_2$, $3B_2O_3$, $4H_2O$, $7Al_2O_3$, $4FeO$, Na_2O.
III. Mg tour.	$12SiO_2$, $3B_2O_3$, $4H_2O$, $5Al_2O_3$, $\frac{28}{3}MgO$, $\frac{2}{3}Na_2O$.

By substituting hydrogen atoms for the metals in these special formulas we obtain:

I. and II.	$H_{60}B_6Si_{12}O_{63}$ or $H_{20}B_2Si_4O_{21}$.
III.	$H_{58}B_6Si_{12}O_{62}$ or $H_{19\frac{1}{3}}B_2Si_4O_{20\frac{2}{3}}$.

Soon after the appearance of Riggs' article, Wülfing* recalculated the results of these twenty analyses and concluded that all tourmalines may be regarded as isomorphous mixtures of two aluminium silicates, "*Alumosilicate*," of the following composition.

I. Alkali tourmaline	$12SiO_2 . 3B_2O_3 . 8Al_2O_3 . 2Na_2O . 4H_2O$,
II. Magnesia tourmaline	$12SiO_2 . 3B_2O_3 . 5Al_2O_3 . 12MgO . 3H_2O$.

In these formulas it is assumed that the isomorphous elements K and Li replace the Na; Fe‴ the Al; and Fe″, Mn and Ca the Mg. By substituting hydrogen atoms for the metals in the foregoing formulas it is found that they both are derivatives of the same acid, $H_{60}B_6Si_{12}O_{63}$ or $H_{20}B_2Si_4O_{21}$. The conclusions derived by Wülfing are that, although in most cases the results of the analyses agree with the percentage values calculated from his formulas, the agreement is not always satisfactory. This he ascribes to the possible need of a

* Mineralogische und petrographische Mittheilungen, x, p. 161.

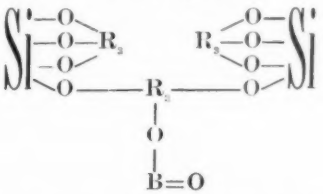
third formula; to possible inaccuracies in the difficult ferrous iron determinations; and in part to the fact, as stated by Riggs, that "the analyses do not represent ideal compounds. . . ." He therefore considers it necessary that further analyses of more carefully selected material should be made.

At about this time also Scharizer* published analyses of three varieties of tourmaline from Schüttenhofen, Bohemia, and discussed his results in connection with the analyses of Riggs. His final conclusion is that, with the exception of the green varieties, tourmalines possess a chemical constitution which can be expressed by the general formula

$$\left[\overset{\text{I}}{\text{R}}_2\overset{\text{II}}{\text{R}}\right]_2\left[\overset{\text{II}}{\text{R}}_3\overset{\text{III}}{\text{R}}_2\right]_4\text{Al}_5(\text{SiO}_3)_{12}\left[\overset{\text{O}}{(\text{BO, HO, F})_2}\right]_7.$$

This formula is certainly difficult to comprehend, and, if we understand it correctly, the univalent radicals BO and HO are isomorphous with fluorine, and these constituents, taken twice, can replace oxygen.

In 1889 Jannasch and Kalb† published the results of nine tourmaline analyses, in which the water and boron were determined directly. These investigators derived from their analyses the general formula $R_9 . BO_2 . (SiO_4)_2$, for which the following structural formula was proposed:



This formula, $R_9 . BO_2 . (SiO_4)_2$, is identical with the one proposed by Riggs, and essentially like the special formula $R'_3Al_2BSi_2O_{10}$ of Rammelsberg. The following special formulas are also given:

I. Li tour. $24SiO_2 . 6B_2O_3 . 15Al_2O_3 . 4FeO . 4(Li_2O, Na_2O) . 7H_2O$
II. Fe tour. $24SiO_2 . 6B_2O_3 . 14Al_2O_3 . 9FeO . 2Na_2O . 7H_2O$
III. Fe-Mg tour. $24SiO_2 . 6B_2O_3 . 13Al_2O_3 12MgO . 2Na_2O . 7H_2O$

These special formulas in their general type are similar to those proposed by Riggs. By substituting hydrogen atoms for the metals they all reduce to one and the same acid, $H_{120}B_{12}Si_{24}O_{126}$ or $H_{20}B_2Si_4O_{21}$.

* Zeitschr. für Kryst., xv, p. 343.

† Berichte der deutschen chemischen Gesellschaft, vol. xxii, p. 216. Also Inaugural Dissertation, Geo. W. Kalb, Göttingen.

There is evidence that Jannasch does not place great confidence in the foregoing formulas, for in Hintze's Mineralogy* the composition is expressed as follows:

I. Lithia tourmaline $Si_{12}O_{63}B_6Al_{15}(Na, Li)_4H_7$
II. Iron tourmaline $Si_{12}O_{67\frac{1}{2}}B_6Al_{14}Fe_9Na_2H_7$
III. Magnesia tourmaline $Si_{12}O_{69}B_6Al_{13}Mg_{12}Na_2H_7$

These formulas are essentially different from the ones first proposed, which may readily be seen by substituting hydrogen atoms for the metals and comparing the resulting acids, as follows:

I. $H_{56}B_6Si_{12}O_{63}$ or $H_{18\frac{2}{3}}B_2Si_4O_{21}$
II. $H_{69}B_2Si_{12}O_{67\frac{1}{2}}$ or $H_{23}B_2Si_4O_{22\frac{1}{2}}$
III. $H_{72}B_2S_{12}O_{69}$ or $H_{24}B_2Si_4O_{23}$

Soon after the appearance of the articles of Riggs and of Jannasch and Kalb, the results of their analyses were recalculated by Goldschmidt,† and the conclusion was reached that tourmaline may be regarded as containing the two following molecules:

I. Alkali tourmaline $R'_{22}R'''_{56}Si_{31}O_{102}$
II. Magnesia tourmaline $R'_{20}R''_{24}R'''_{44}Si_{31}O_{102}$

These formulas are both derived from an acid $H_{200}Si_{31}O_{102}$ or $H_{6.45}SiO_{3.29}$.

In 1893 Rheineck,‡ after calculating the results of the many tourmaline analyses, concluded that the composition of all tourmalines may be expressed by formulas of the following type, in which Al_4 appears as a constant:

I. Alkali tourmaline $Al_4Si_3BH_3O_{15}$
II. Alkali tourmaline $Al_4Si_3B_2H_4O_{17}$
III. Magnesia tourmaline $Al_4Si_5B_2M_4H_4O_{25}$, etc.

M represents the bivalent metals Fe, Mn, Mg and Ca. H includes Na, Li and K. Among the numerous examples he stated that the composition of the black tourmaline from Pierrepont, N. Y., may be represented by either of the following expressions:

$$\begin{cases} 114\ Al_4Si_5B_2M_4H_4O_{25} \\ 10\ Al_4Si_2B_6O_{25} \end{cases} \quad \text{or} \quad \begin{cases} 10\ Al_4Si_2B_2H_6O_{15} \\ 93\ Al_4Si_5B_2M_4H_4O_{25} \\ 21\ Al_4Si_5B_4M_4O_{26} \end{cases}$$

* Vol. ii, p. 311 (communication from manuscript by Jannasch).
† Zeitschr. für Kryst, xvii, pp. 52 and 61.
‡ Zeitschr. für Kryst., xxii, p. 52.

By substituting hydrogen atoms for the metals in these expressions, and multiplying by the factors, 114 and 10 in the one case, and 10, 93 and 21 in the other, the acids become $H_{2666}B_{266}Si_{600}O_{2100}$ and $H_{2832}B_{930}Si_{666}O_{2051}$, or, when simplified, $H_{19.0}B_{1.9}Si_4O_{20.6}$ and $H_{18.9}B_{1.9}Si_4O_{20.5}$. The improbable nature of such acids is evident. In the opening paragraph of his article Rheineck stated that the obscure and complex chemical relations of this mineral have necessitated a series of speculations and calculations extending somewhat interruptedly over a period of many years, in order to arrive at results such as those embodied in the foregoing formulas.

In 1895 Clarke* discussed the constitution of tourmaline and proposed the following formulas:

1.

$$\begin{array}{l} \quad SiO_4 = R'_3 \\ Al - SiO_4 = Al \\ \quad SiO_4 = Al - BO_3 \\ \qquad\qquad | \\ \qquad Al - BO_3 = NaH \\ \qquad\qquad | \\ \quad SiO_4 = Al - BO_3 \\ Al - SiO_4 = Al \\ \quad SiO_4 = Al \end{array}$$

2.

$$\begin{array}{l} \quad SiO_4 = MgH \\ Al - SiO_4 = MgH \\ \quad SiO_4 = Al - BO_3 \\ \qquad\qquad | \\ \qquad Al - BO_3 = NaH \\ \qquad\qquad | \\ \quad SiO_4 = Al - BO_3 \\ Al - SiO_4 = Al \\ \quad SiO_4 = Al \end{array}$$

3.

$$\begin{array}{l} \quad SiO_4 = MgH \\ Al - SiO_4 = MgH \\ \quad SiO_4 = Al - BO_3 \\ \qquad\qquad | \\ \qquad Al - BO_3 = NaH \\ \qquad\qquad | \\ \quad SiO_4 = Al - BO_3 \\ Al - SiO_4 = MgH \\ \quad SiO_4 = Al \end{array}$$

4.

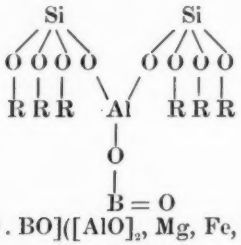
$$\begin{array}{l} \quad SiO_4 = MgH \\ Al - SiO_4 = MgH \\ \quad SiO_4 = Al - BO_3 \\ \qquad\qquad | \\ \qquad Al - BO_3 = NaH \\ \qquad\qquad | \\ \quad SiO_4 = Al - BO_3 \\ Al - SiO_4 = MgH \\ \quad SiO_4 = MgH \end{array}$$

Clarke assumes variations from these formulas in that Fe‴ and Cr can replace the Al; Fe″ and Mn the Mg; Ca the NaH; and small amounts of F the BO_3. Proof of a constitution corresponding to the formulas cannot of course be expected, but it is doubtful whether aluminium could exercise such varied functions as the formulas indicate. The grounds for believing that fluorine can replace BO_3 are not stated. The acid from which all these formulas are derived is $H_{29}B_3Si_6O_{31}$ or $H_{1\frac{1}{2}}B_2Si_4O_{20\frac{2}{3}}$.

Lastly Groth† has adopted the formula of Jannasch $[SiO_4]_3 . BO_3 . R'_3$, but interprets it as follows:

* Bulletin of the U. S. Geological Survey, No. 125, p. 56.

† Tabellarische Uebersicht der Mineralien, 4te Auflage, 1898, p. 117.



or $[SiO_4]_2[AlO \cdot BO]([AlO]_2, Mg, Fe, Na_2, Li_2, H_2)_3$

That the univalent radical [AlO] can replace R′ does not appear in the original article of Jannasch, and it makes a decided difference whether three R's are replaced by one atom of Al or by three [AlO] radicals. The latter assumption implies a basic character which tourmaline does not possess.

We have thus reviewed the work already done in order to show the difficulties which this problem has presented. It is, however, interesting to note how closely different investigators come to one type of acid from which all varieties of tourmaline are derived. For the sake of comparison these acids have been reduced to four silicon atoms, and are given below, both as borosilicic acids and with the boron replaced by hydrogen.

Rammelsberg	$H_{18}B_2Si_4O_{20}$	or	$H_{24}Si_4O_{20}=H_6SiO_5$
	$H_{18\cdot66}B_{1\cdot77}Si_4O_{20}$	or	$H_{24}Si_4O_{20}$
Riggs	$H_{18}B_2Si_4O_{20}$	or	$H_{24}Si_4O_{20}$
	$H_{20}B_2Si_4O_{20}$	or	$H_{26}Si_4O_{20}$ (Irrational)
	$H_{20}B_2Si_4O_{21}$	or	$H_{26}Si_4O_{21}$
	$H_{19\cdot33}B_2Si_4O_{20\cdot66}$	or	$H_{25\cdot33}Si_4O_{20\cdot66}$
Jannasch and Kalb	$H_{18}B_2Si_4O_{20}$	or	$H_{24}Si_4O_{21}$
	$H_{20}B_2Si_4O_{21}$	or	$H_{26}Si_4O_{20}$
Wülfing	$H_{20}B_2Si_4O_{21}$	or	$H_{26}Si_4O_{21}$
Goldschmidt			$H_{25\cdot8}Si_4O_{20\cdot9}$
Rheineck	$H_{19\cdot0}B_{1\cdot9}Si_4O_{20\cdot6}$	or	$H_{24\cdot7}Si_4O_{20\cdot6}$ (Irrational)
	$H_{18\cdot9}B_{1\cdot9}Si_4O_{20\cdot3}$	or	$H_{24\cdot6}Si_4O_{20\cdot3}$ etc.
Clarke	$H_{19\cdot33}B_2Si_4O_{20\cdot66}$	or	$H_{25\cdot33}Si_4O_{20\cdot66}$

New Analyses.

Method of analysis.—The present investigation was undertaken with the expectation that for the solution of the problem in hand it would probably not be necessary to make a long series of analyses but rather *exceedingly accurate* analyses of a few carefully selected types of tourmaline. We therefore prefaced our work by a careful study of those features of the tourmaline analysis, which have proved most difficult. The method proposed by Gooch* of distilling off the boron with methyl alcohol and weighing it as calcium borate is very exact,

* Amer. Chem. Jour., ix, p. 23.

but its application to an insoluble silicate, especially one containing fluorine, needed careful study. Mixtures were accordingly made of silicates to which weighed quantities of borax and fluorite were added and the following conditions were determined, which yielded the most accurate boron determinations. The mineral was fused with from four to five parts of sodium carbonate, the fusion extracted with water, and, without filtering, an excess of ammonium carbonate was added. The insoluble residue and the precipitate were filtered off, the filtrate concentrated, acidified slightly with nitric acid and distilled with methyl alcohol. The residue from the sodium carbonate fusion together with the precipitate produced by the ammonium carbonate was fused again with sodium carbonate, treated with water, filtered and distilled with methyl alcohol after acidifying with nitric acid. About one half of one per cent of boric oxide was obtained from the second treatment, and in no case did we succeed in obtaining an exact determination of the boric oxide without repeating the fusion. The weighed mixture of calcium borate and oxide was in all cases found to contain a small amount of fluorine. It was therefore dissolved in hydrochloric acid, and part of the lime together with calcium fluoride was precipitated with sodium carbonate. The precipitate was ignited, treated with acetic acid and the resulting calcium fluoride weighed. The amount of fluorine thus found never amounted to over 0·20 per cent.

Fluorine was determined by the modified Berzelius method described by Penfield and Minor.*

Water was determined by fusing the mineral with sodium carbonate in a combustion tube and collecting the water in a weighed tube containing sulphuric acid, a method which has been thoroughly tested and is known to give reliable results.†

For the determination of the bases the mineral was decomposed by fusion with sodium carbonate and the silica separated as usual. It was found by experiment that the amount of silica volatilized by the small amount of fluorine in the mineral could practically be neglected. In one variety of tourmaline two determinations of silica made by the Berzelius method of fusing the mineral and a weighed amount of silica with sodium carbonate, and separating the silica with ammonium carbonate and an ammoniacal solution of zinc oxide, gave 36·69 and 36·76 per cent, while determinations by the ordinary method gave 36·75 and 36·73 per cent. A similar conclusion, that when the amount of fluorine is small it is not necessary to separate the silica by the Berzelius method, was also reached by Riggs.

* This Journal, III, xlvii, 1894, p. 387.
† This Journal, III, xlviii, 1894, p. 31.

The filtrate from the silica was evaporated to dryness, moistened with hydrochloric acid and repeatedly evaporated with methyl alcohol to remove all possibilities of boric oxide being precipitated with the bases and thus increasing their weight.

For the determination of the alkalies the Smith fusion was employed and, after removal of ammonium salts, the residue was treated with acid and methyl alcohol and evaporated to remove any borate that might possibly be present. Lithium was separated by the Gooch method of boiling with amyl alcohol,* and was finally weighed as sulphate.

It was proved by careful qualitative tests† that the iron was ferrous, and that, at the most, not more than traces of ferric iron could be present. This statement holds good not only for the varieties analyzed, but for all the varieties of black tourmaline which were accessible to us.

Selection and preparation of material.—One of the varieties selected for analysis was the white or colorless tourmaline from De Kalb, St. Lawrence Co., New York. This was chosen because according to the analysis of Riggs it represented almost the extreme type of a magnesia tourmaline, and, containing almost no iron, there could be no appreciable error from a failure to estimate that constituent correctly. The material was derived in part from a specimen in the Brush Collection and in part from specimens collected by one of us (Penfield) while connected with the U. S. Geological Survey. The clear, colorless, glassy material was most carefully selected with the aid of a lens, ground and sifted to a uniform grain, and suspended in methylene iodide. The specific gravity was uniform, and the portion used for the analysis floated at 3·065 and sank at 3·033. As an additional precaution the grains were treated with a mixture of hydrochloric and hydrofluoric acids, which have almost no action even on finely pulverized tourmaline, in order to remove any possible traces of adhering calcite, tremolite or pyroxene, although these were not seen nor believed to be present. It may be stated concerning the final product that probably it was as pure as it is possible to get a mineral substance.

Another variety selected for analysis was from the feldspar quarries at Haddam Neck on the Connecticut River. Wonderful tourmalines have recently been obtained from this locality, and they are already well know to most collectors. We are indebted for our supply of material to Mr. Ernest Schernikow of New York, who generously placed at our disposal an almost unlimited supply of crystals of gem quality. We selected small prisms, 2 to 4^{mm} in diameter, of a uniform rather pale green color. They were of ideal purity, perfectly transparent

* Amer. Chem. Jour., ix, p. 33.

† See note, p. 124.

and without flaws. Any traces of foreign material that might possibly be adhering to their outer surfaces were removed by treating them for a considerable time with hydrofluoric acid. The specific gravity, taken with the chemical balance, was found to be 3·089.

We were prepared to extend our investigation by analyzing other varieties, but having completed the above mentioned two and finding that the results corresponded with those of other investigators, it was decided that the data which would be derived from further analyses would probably add very little to the knowledge which we already possess.

The results of the analyses are as follows:

COLORLESS TOURMALINE, DE KALB, N. Y.

	I.	II.	Average.			Riggs.
SiO_2	36·69	36·76	36·72÷60=	·612	4·00	36·88
TiO_2	·06	·05	·05			·12
B_2O_3	10·86	10·77	10·81÷70=	·154	1·01	10·58
Al_2O_3	29·75	29·61	29·68÷17=1·741			28·87
FeO	·23	·21	·22÷36= ·006			·52
MgO	14·91	14·92	14·92÷20= ·746			14·53
CaO	3·47	3·50	3·49÷28= ·125	3·042	19·90	3·70
Na_2O	1·29	1·23	1·26÷31= ·040			1·39
K_2O	·07	·03	·05÷47= ·002			·18
H_2O	2·98	....	2·98÷ 9= ·331			3·56
F	·92	·95	·93÷19= ·049			·50
			101·11			100·83
O equivalent to F			·39			·21
			100·72			100·62

GREEN TOURMALINE, HADDAM NECK, CONN.

	I.	II.	Average.			Brazil. Riggs.
SiO_2	36·87	37·05	36·96÷60 =	·616	4·00	37·39
TiO_2	·03	·03	·03			?
B_2O_3	11·09	10·92	11·00÷70 =	·157	1·02	10·29
Al_2O_3	39·53	39·59	39·56÷17 =2·327			39·65
FeO	2·12	2·15	2·14÷36 = ·059			*2·42
MnO	1·96	2·04	2·00÷35·5= ·056			1·47
MgO	·15	·15	·15÷20 = ·008			none
CaO	1·32	1·25	1·28÷28 = ·046	3·078	19·98	·49
Na_2O	2·13	2·06	2·10÷31 = ·068			†2·67
Li_2O	1·65	1·63	1·64÷15 = ·110			1·71
H_2O	3·14	3·06	3·10÷ 9 = ·344			3·63
F	1·09	1·17	1·13÷19 = ·060			·32
			101·09			100·04
O equivalent to F			·48			·13
			100·61			99·91

* Includes 0·15 per cent. Fe_2O_3. † Includes 0·25 per cent. K_2O.

On treating the analyses according to the customary method of deriving a formula (dividing each constituent by its molecular weight and finding the ratio of the quotients) it was found that although the SiO_2 and B_2O_3 were present in the proportion of 4:1, no definite relation could be detected between the silica, the different kinds of oxides, and the water. It was decided, therefore, to determine the relative number of hydrogen atoms equivalent to the metals and thus learn the acid from which tourmaline is derived. This was readily accomplished by dividing the constituents by appropriate fractions of their molecular weights; for example, since the aluminium atoms in Al_2O_3 replace six hydrogens, the quantity of Al_2O_3 was divided by one-sixth of its molecular weight, the FeO by one half of its molecular weight, etc. Since fluorine is regarded as playing the same role as hydroxyl, its ratio was added directly to that of the hydrogen. The result of this treatment is very satisfactory. The first analysis gives the ratio of $SiO_2 : B_2O_3 : H = 4:1:19{\cdot}90$, and the second $4:1{\cdot}02:19{\cdot}98$. Both ratios approximate so closely to 4:1:20 that there can be no reasonable doubt that the acid from which these tourmalines are derived is $H_{20}B_2Si_4O_{21}$. This formula may seem at first somewhat complex, but it is not especially so for a boro-silicic acid. It can not be simplified by division, and it is based upon the very best kind of evidence, namely, the close approximation to rational numbers of the two ratios, which are derived from widely separated types of tourmaline.

Before discussing the possible constitution of this acid, it will be shown to what extent the analyses of other investigators confirm the results obtained by us.

Review of Rammelsberg's Analyses.—The analyses appear with certain variations in his different publications, and the results which will be discussed here are given in his *Mineralchemie*, 1875. These are quoted in the sixth edition of Dana's Mineralogy, and where there is occasion to refer to individual analyses they will be designated by the numbers assigned to them in the latter work. The same plan also will be adopted for the analyses of Riggs, Jannasch and Kalb and others. Thirty-five analyses are given by Rammelsberg, of which No. 34 is not complete.

Adopting the same method of calculation as applied to our own analyses, and using one-fourth of the silica as unity, the ratios of $SiO_2 : B_2O_3$ were found to vary between $4:1{\cdot}21$ and $4:0{\cdot}71$, and the ratios of SiO_2 to the total hydrogen atoms between $4:16{\cdot}5$ and $4:19{\cdot}7$. The result of grouping the ratios of the hydrogen atoms is as follows:

Limits of variation,	16·5—17·5	17·5—18·5	18·5—19·5	19·5—19·7
Number of analyses,	8	12	12	2

The ratios of SiO_2 to the total hydrogen atoms show a wide variation, and the hydrogens for the most part fall far below 20, which is required by the new formula. Rammelsberg, however, claims that boron plays the part of a metal, replacing aluminium, and that all tourmalines are derivatives of an acid H_8SiO_5 or $H_{24}Si_4O_{20}$. Replacing, therefore, the boron by hydrogens (B_2O_3 is equivalent to $3H_2O$), it is found that the ratios of SiO_2 to the total hydrogens then vary from 4 : 21·9 to 4 : 25·1. The result of grouping the ratios is as follows:

Limits of variation,	21·9—22·5	22·5—23·5	23·5—24·5	24·5—25·1
Number of analyses,	3	10	17	4

The ratio of SiO_2 to the total hydrogens demanded by Rammelsberg's formula is 4 : 24, and in only seventeen, or one-half, of the analyses are the ratios $24 \pm 0{\cdot}5$, while they are reasonably sharp, $24 \pm 0{\cdot}2$, in only seven cases. It would seem therefore that owing to certain defects the analyses fail to give decisive results. The ratios do not satisfactorily support Rammelsberg's formula nor the one which we have proposed. In his latest publications* Rammelsberg claims great accuracy both for his analyses and for the analytical methods which he employed, and in justice to him it does not seem right to ignore his results without endeavoring to discover the possible defects of the analyses and the influences exerted by them upon the ratios. In the first place, it is believed, for the following reasons, that his silica determinations are too high: it is presumable that facilities were not at hand for producing the intense heat necessary for expelling the last traces of water from the silica; there is no statement that the silica was tested as to its purity by volatilization with hydrofluoric acid; and, lastly, a little silica might have been derived from glass beakers and even from the distilled water, provided it was kept in glass bottles or carboys. It is certain that the water determinations are too low, and this is admitted by Rammelsberg. It is well known that when a silicate containing fluorine and hydroxyl is heated some hydrofluoric acid is liberated, and if the experiment is tried in a closed tube the glass is etched, while probably the mineral also is attacked with the formation of silicon fluoride. Rammelsberg,† however, points out that only a portion of the fluorine is thus expelled, and since the amount of fluorine in tourmaline is small, the loss on ignition should give a fair estimate of the amount of water which the mineral contains. Loss on ignition seems to have been very carefully determined by Rammelsberg, and in those analyses in which

* Berlin Akademie, 1890. Mineralchemie, Zweites Supplement, 1895.
† Mineral Chemie, Zweites Supplement, p. 284.

fluorine is estimated the water is given as equal to the loss on ignition *less either the fluorine or the silicon fluoride equivalent to it*, while when no fluorine was determined a quantity is *assumed*, usually one-third to one-half of one per cent, and this quantity or the silicon fluoride equivalent to it is deducted from the loss on ignition. In the latter case the *assumed* quantity of fluorine never appears in the results as a constituent of the mineral. Again, no account seems to have been taken of the fact that on prolonged ignition the ferrous iron may become oxidized to ferric, thus causing the water determinations to be too low. In this connection it is interesting to refer to some results obtained by Riggs, who has given with many of his analyses both the loss on ignition and the direct water determinations. When much ferrous oxide is present the loss on ignition is less than the water, but when this loss is increased by an amount equivalent to the oxygen which the iron present can take up in changing from ferrous to ferric oxide, the results become almost equal. The results, in fact, would almost do for duplicate determinations, as shown below:

Number	36	37	38	41	42	44	45	46	47	48	49	50	51
Increase of O.	·03	·06	·15	·35	·72	1·34	1·58	1·52	1·32	·94	·91	·91	·42
Loss on ign.	4·35	4·10	4·09	3·62	3·31	2·30	2·17	2·19	2·41	2·88	2·86	2·69	3·59
	4·38	4·16	4·24	3·97	4·03	3·64	3·75	3·71	3·73	3·82	3·77	3·60	4·01
H_2O direct	4·26	3·90	4·16	3·64	3·49	3·69	3·62	3·49	3·62	3·63	3·60	3·34	3·79

We cannot agree with Rammelsberg that the method adopted by Riggs for determining water directly gives too high results, for it has been abundantly proved that when properly executed it gives exceedingly accurate ones. It is safe to assume, therefore, that if the determinations of the loss on ignition as given by Rammelsberg are corrected for the oxidation of the iron, the results will furnish fair estimates of the percentages of water.

Accepting as an established fact that SiO_2 and B_2O_3 are always present in tourmaline in the proportion 4:1, Rammelsberg's results may be modified by correcting the water determinations and estimating both SiO_2 and B_2O_3 by difference, thus distributing the errors of analyses upon two constituents, rather than upon the B_2O_3 alone. Below are given the results of applying this method of correction to seven of Rammelsberg's analyses made upon varieties of tourmaline which have subsequently been investigated by either Riggs or Jannasch and Kalb. There are also given for comparison the analyses of the other investigators and Rammelsberg's figures for SiO_2, H_2O and loss on ignition.

		Gouverneur, N.Y., Brown.		Monroe, Conn., Brownish-Black.		Haddam, Conn., Black.		Snarum, Black.	
		Rm. 1.	Rgs. 53.*	Rm. 7.	Rgs. 51.	Rm. 11.	Rgs. 47.	Rm. 12.	J. & C. 56.
Corrected.	TiO_2	---	1·19	---	1·61	---	·57	---	1·10
	SiO_2	[35·76]	37·39	[36·40]	36·41	[34·75]	34·95	[34·56]	35·64
	B_2O_3	[10·43]	10·73	[10·61]	9·65	[10·14	9·92	[10 08]	9 93
	Al_2O_3	31·32	27·79	31·18	31·27	30·87	31·11	30·00	29 41
	Fe_2O_3	----	·10	----	----	----	·50	----	2·90
	FeO	1·14	·64	4 07	3·80	8·54	11·87	11·16	6·56
	MnO	----	----	----	----	----	·09	----	----
	MgO	14·89	14·09	9·90	9·47	8·60	4·45	7·94	8·00
	CaO	1·60	2·78	1·81	·98	1·33	·81	·65	1·65
	Na_2O	1·28	1·72	1·82	2·68	1·60	2·22	1·13	3·03
Corrected.	K_2O	·26	·16	·44	·21	·73	·24	·53	·16
	H_2O	3·32	3·83	3·77	3·79	3·44	3·62	3·63	2·94
	F	----	----	----	----	----	----	·55	----
		100·00	100·42	100·00	99·87	100·00	100 35	100·23	101·32
Original.	SiO_2	38·85		39·01		37·50		37·22	
	H_2O	2·31		2·82		1·81		1·64	
	Ign	3·19		3·32		2·49		2·39	

		Alabashka, Black.			Brazil, Green.	Pierrepont, N. Y., Black.		
		Rm. 20.	J. & C. 57.	Rm. 32.	Rgs. 41.	J. & C. 64.	Rm. 35.	Rgs. 50.
Corrected.	TiO_2	---	----	----	----	----	----	·55
	SiO_2	[35·44]	35·41	[35·90]	36 91	37·05	[34·98]	35·61
	B_2O_3	[10·33]	10·14	[10·51]	9·87	9·09	[10·20]	10·15
	Al_2O_3	30·41	33·75	37·81	38·13	40·03	27·18	25·29
	Fe_2O_3	----	----	----	·31	----	----	·44
	FeO	15·59	13·42	5·83	3·19	2·36	9·08	8·19
	MnO	·54	----	1·13	2·22	2·35	----	----
	MgO	1·88	1·57	·92	·04	·32	10·13	11·07
	CaO	----	·17	----	·38	·47	2·91	3·31
	Na_2O	1·02	2·08	2·21	2·70	3·18	1·50	1·51
	K_2O	·47	·34	·42	·28	----	----	·20
	Li_2O	----	----	1·30	1·61	·60	----	----
	H_2O	3·88	3·41	3·57	3·64	3·23	4·02	3·34
	F	·76	·28	·70	·14	1·15	----	·27
		100·32	100·57	100·30	99·42	99·83	100·00	99·93
Original.	SiO_2	36·19		38·06			36·64	
	H_2O	1·11		2·23			3·01	
	Ign	2·15		2·92			?	

With the present interpretation of Rammelsberg's analyses the ratios of SiO_2 : B_2O_3 have been assumed as 4 : 1, while those of SiO_2 to the total equivalent of hydrogen atoms in the different analyses are as follows:

No. 1	No. 7	No. 11	No. 12	No. 20	No. 32	No. 35
4 : 20·7	4 : 19·8	4 : 20·5	4 : 20·06	4 : 19·6	4 : 19·9	4 : 20·2

*Compare the reference to this analysis on p. 115.

The agreement between the corrected analyses of Rammelsberg and those of the other investigators is very remarkable, and the ratios of SiO_2 to the total equivalent of hydrogen atoms approximate closely to 4 : 20 (the average is 4 : 20·1).

Seven complete analyses are also given by Rammelsberg and to them corrections for water have been applied, while the errors of the analysis have been distributed upon the SiO_2 and B_2O_3. The results are given below, together with Rammelsberg's figures for SiO_2, B_2O_3, H_2O and loss on ignition:

No. of Analysis,		2	5	22	24	29	31	33
Corrected.	SiO_2	[36·53]	[36·37]	[34·82]	[34·87]	[35·49]	[36·03]	[36·02]
	B_2O_3	[10·66]	[10·61]	[10·16]	[10·17]	[10·35]	[10·51]	[10·51]
	Al_2O_3	32·90	33·15	35·46	33·35	42·63	44·05	36·80
	FeO	·66	2·88	13·17	11·95	----	----	6·38
	MnO	----	----	·28	1·25	1·94	·92	·78
	MgO	11·79	10·89	1·52	·63	·39	·20	1·88
	CaO	1·25	·77	----	----	·45	----	----
	Na_2O	2·37	1·52	·98	1·75	2·60	2·00	2·47
	K_2O	·47	----	·09	·40	·68	1·30	·47
Corrected.	Li_2O	----	----	----	·84	1·17	1·22	·72
	H_2O	3·00	3·81	3·28	4·31	3·61	3·37	3·65
	F	·64	----	·41	·82	1·18	·70	·55
		100·27	100·00	100·17	100·34	100·49	100·30	100·23
Original.	SiO_2	38·09	38·33	36·11	36·22	38·19	38·85	38·46
	B_2O_3	11·15	9·86	11·64	10·65	9·97	9·52	9·73
	H_2O	2·05	2·81	1·26	2·21	2·00	2·41	2·31
	Ign.	2·93	3·49	1·82	2·98	3·61	3·37	2·94

A comparison of the corrected analyses with the figures given by Rammelsberg indicate that B_2O_3 has been determined with a good degree of accuracy. His water is always low and his silica high. The ratios of SiO_2 to the total equivalent of hydrogen atoms in the corrected analyses are as follows:

	No. 2	No. 5	No. 22	No. 24	No. 29	No. 31	No. 33
Ratio	4 : 20·0	4 : 20·3	4 : 20·4	4 : 20·7	4 : 21·8	4 : 21·4	4 : 20·2

Two of the hydrogen ratios are very high; four of them approximate closely to 4 : 20·0; the average is 20·7.

The results obtained by applying similar corrections to the remaining twenty analyses are given in the table on page 113, together with Rammelsberg's figures for SiO_2, H_2O and loss on ignition. In the last column the ratios of the total equivalent of hydrogen atoms are given, one quarter of the corrected SiO_2 being taken as unity.

The ratios of the silica to the hydrogen atoms in these twenty analyses exhibit a rather wide variation, from 4 : 18·7 to 4 : 21·8. The average, however, is 4 : 20·4, and the average for all of his thirty-four analyses is also 4 : 20·4, or approximately 4 : 20.

No.	Locality.	Corrected. SiO_2	Corrected. B_2O_3	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Li_2O	Corrected. H_2O	F	Original. SiO_2	Original. H_2O	Original. Ign.	Ratio.
3	Eibenstock	[35·41]	[10·32]	30·86	4·36	....	11·62	0·88	2·27	0·30	....	3·98	....=100·00	37·75	2·82	3·50	20·8
4	Zillerthal	[36·39]	[10·62]	32·55	2·80	0·36	10·46	0·16	2·13	0·37	....	3·85	0·36=100·15	38·51	3·04	3·54	20·1
6	Texas, Pa.	[35·76]	[10·43]	34·56	2·98	0·09	9·11	0·71	2·00	0·73	....	3·63	....=100·00	38·45	2·80	3·30	20·6
8	Godhaab	[34·47]	[10·06]	34·26	4·42	....	9·51	1·25	2·00	0·43	....	3·60	....=100·00	37·70	2·61	3·11	21·8
9	Havredal	[34·88]	[10·18]	31·26	7·58	....	9·43	0·80	1·78	0·32	....	3·77	....=100·00	37·11	2·43	2·93	20·9
10	St. Gothard	[36·40]	[10·62]	31·41	7·23	....	7·27	1·31	1·43	0·28	....	4·05	....=100·00	38·00	2·75	3·25	19·5
13	Elba	[35·48]	[10·35]	30·02	9·93	0·58	6·77	0·72	2·19	0·25	....	3·60	0·15=100·06	38·20	2·29	2·50	19·6
14	Unity, N. H.	[33·57]	[9·79]	30·44	13·23	....	6·32	1·02	1·94	....	....	3·69	....=100·00	36·29	1·72	2·22	21·3
15	Krumman	[34·38]	[10·03]	34·12	11·58	....	3·84	0·44	1·36	0·30	....	3·95	....=100·00	36·43	2·11	2·66	21·2
16	DeKalb, N. Y.	[34·65]	[10·11]	31·86	12·55	0·51	3·49	....	2·04	0·30	....	4·31	0·31=100·13	37·07	2·48	2·92	20·7
17	Langenbeilau	[35·94]	[10·48]	31·63	11·64	....	3·65	0·62	1·93	0·82	....	3·29	....=100·00	37·24	1·45	2·00	18·9
18	Bovey Tracy	[36·01]	[10·50]	30·22	13·82	0·40	2·62	0·50	1·39	0·65	....	3·63	0·45=100·19	37·94	1·74	2·09	18·7
19	Krumbach	[33·96]	[9·90]	32·21	12·82	1·50	2·32	0·40	1·43	0·46	....	4·63	0·64=100·27	36·25	2·34	3·21	21·3
21	Andreasberg	[34·05]	[9·93]	30·34	17·40	0·11	0·78	0·72	1·36	0·58	....	4·24	0·85=100·36	36·06	1·54	2·31	20·5
23	Sarapulsk	[36·92]	[10·77]	31·53	10·30	2·68	1·06	....	2·37	0·33	....	3·58	0·80=100·34	38·30	1·81	2·44	18·8
25	Elba	[34·40]	[10·03]	34·15	10·52	1·87	1·68	....	2·30	0·75	0·32	3·71	0·47=100·20	37·14	1·90	2·54	20·8
26	Elba	[35·81]	[10·45]	33·19	5·43	3·59	4·30	0·30	2·04	0·38	....	3·94	0·98=100·41	38·24	2·00	3·34	20·1
27	Elba	[36·09]	[10·52]	41·89	1·38	2·51	0·41	....	2·40	0·34	0·74	3·43	0·50=100·21	37·74	2·60	3·28	20·9
28	Shaitansk	[35·64]	[10·40]	43·97	....	1·53	1·62	0·62	1·53	0·21	0·48	3·59	0·70=100·29	38·26	2·49	3·59	21·8
30	Rozena	[37·15]	[10·84]	41·83	....	0·95	0·61	....	1·37	2·17	0·41	3·98	1·19=100·50	41·16	2·57	3·98	20·3

As already stated, Rammelsberg admits that his water determinations are too low; he also states that the formula for a complex mineral like tourmaline cannot be determined from a few analyses but must be derived rather from the average of many determinations. If then it may be assumed that his loss on ignition, when corrected for the oxidation of the iron, gives a close approximation to the amount of water, his results on the whole agree with the formula $H_{20}B_2Si_4O_{21}$. It may also be stated that if the analyses are not corrected they lead to no satisfactory formula.

Review of Riggs' Analyses.—Twenty analyses of American tourmalines were made by Riggs, and the ratios derived from them furnish the very best evidence of the accuracy of his results. The ratios are as follows:

No.	SiO_2 :	B_2O_3 :	Total hydrogen.	No.	SiO_2 :	B_2O_3 :	Total hydrogen.
36.	4 :	0·90 :	20·2	46.	4 :	0·96 :	20·2
37.	4 :	0·93 :	20·5	47.	4 :	0·98 :	20·08
38.	4 :	0·92 :	19·5	48.	4 :	1·01 :	20·06
39.	4 :	0·94 :	19·7	49.	4 :	1·01 :	20·12
40.	4 :	0·96 :	19·3	50.	4 :	0·98 :	19·2
41.	4 :	0·92 :	19·7	51.	4 :	0·91 :	19·6
42.	4 :	0·97 :	19·8	52.	4 :	0·94 :	20·11
43.	4 :	0·94 :	20·03	53.	4 :	0·97 :	18·9
44.	4 :	0 88 :	20·2	54.	4 :	0·98 :	19·8
45.	4 :	0·95 :	20·03	55.	4 :	1·01 :	20·6

The average of these ratios is 4 : 0·95 : 19·88, or a very close approximation to 4 : 1 : 20, which indicates that tourmaline is derived from the acid $H_{20}B_2Si_4O_{21}$. It is pointed out by Riggs that "the boric acid found invariably falls short of the theory." This is generally, though not always, the case, and it is presumed that this slight defect in the analyses is due to the fact that it is not always possible to obtain a correct determination of boric oxide by the Gooch method without a second fusion of the silicate with sodium carbonate, which Riggs does not mention having made. It is not indicated by the ratios that these analyses "give as a general tourmaline formula the simple boro-orthosilicate $R_9BO_2 2SiO_4$" suggested by Riggs. The nearest approach to this is analysis No. 53, in which the ratio of SiO_2 to the total hydrogen is 4 : 18·9. The ratios with few exceptions show a very close approximation to the rational numbers 4 : 1 : 20. In eleven cases the numbers for the hydrogen ratios vary between the narrow limits 19·8 and 20·2. How exact the analyses must be in order to yield such ratios may be best understood when it is known that a difference of one-half of one per cent in the estimation of either silica or water would

change the numbers of the hydrogen ratio ± 0·27 in the one case and ± 0·38 in the other. If the silica were one-half of one per cent high and the water correspondingly low, the effect upon the ratio would be to change it from 4 : 1 : 20 to 4 : 0·99 : 19·35. The evidence is therefore convincing that, with the exception of analysis No. 53 (brown tourmaline from Gouverneur, N. Y.), the analyses of Riggs are very exact, and also that the material he analyzed was very pure.* Referring to page 111, it will be observed that analysis No. 53 is the one which compares most unfavorably with Rammelsberg's corrected analyses. If the silica in this analysis were 1·25 per cent lower and the Al_2O_3 correspondingly higher, the agreement with Rammelsberg's corrected analysis would be quite satisfactory, and the ratio would correspond with the theory. Leaving out of consideration this one analysis, which may be considered as either defective or made upon impure material, the average of the ratios of Riggs' analyses becomes 4 : 0·95 : 19·91.

The analyses of Riggs were very severely criticized by Rammelsberg, who characterized tourmaline analysis as "*Kein Thema für Anfänger*," but in the light of our present investigation we find the results very accurate, and it may justly be said that we are indebted to Riggs for the best series of tourmaline analyses that has ever been made. In fact, our conclusions regarding the composition of the mineral might readily have been deduced from his results alone.

Review of the analyses of Jannasch and Kalb.—Nine analyses were made, from which the following ratios have been calculated:

No.	SiO_2	:	B_2O_3	:	Total hydrogen.	No.	SiO_2	:	B_2O_3	:	Total hydrogen.
56.	4	:	0·96	:	19·7	61.	4	:	0·95	:	20·2
57.	4	:	0·99	:	19·8	62.	4	:	0·80	:	20·00
58.	4	:	0·95	:	20·4	63.	4	:	0·98	:	19·7
59.	4	:	0·92	:	18·8	64.	4	:	0·84	:	20·01
60.	4	:	0·88	:	20·4	Average,	4	:	0·92	:	19·9

These analyses, like those of Riggs, bear every evidence of having been made with great precision, and the ratios, with the single exception of No. 59, approximate closely to 4 : 1 : 20, thus furnishing additional evidence that the acid from which all tourmalines are derived is $H_{20}B_2Si_4O_{21}$. The analyses do not

* In a personal communication from Professor Riggs the following statement is made concerning the quality of the material investigated by him: "The material analyzed was of excellent quality, selected with great care. The colorless, pink and light green varieties were transparent, gem-like crystals, and the material of the rose-colored, brown and black varieties was, in my opinion, equally pure." Dated, Hartford, January 4th, 1899.

indicate the general formula $R_9 . BO_3 . 2SiO_4$, proposed by Jannasch and Kalb. Their boric oxide determinations are in all cases a trifle too low for the theory, but it is believed that the reason for this is to be sought in imperfections of the method* for determining this constituent in a complex silicate. The analyses are excellent, and they rank with those of Riggs, among the best analyses of tourmaline that have been made. From our own experience, however, it is very questionable whether tourmaline contains so much ferric iron as recorded in some of these analyses (2·90 to 6·68 per cent).

THE ANALYSES OF SCHARIZER.—The ratios of the three analyses are as follows:

No.	SiO_2 :	B_2O_3 :	Total hydrogen.
65	4 :	0·70 :	20·9
66	4 :	0·76 :	21·0
67	4 :	0·74 :	20·2

By comparing these ratios with the ones which have been previously considered, it would seem that there are good grounds for believing that in these analyses the B_2O_3 determinations are too low, and that the bases have not been determined with extreme accuracy. The ratios of SiO_2 to the total hydrogen atoms in the main substantiate the formula $H_{20}B_2Si_4O_{21}$.

ANALYSES FROM MISCELLANEOUS SOURCES.—In looking over the literature a number of analyses have been found which need to be recorded. They have been made partly for the purpose of identifying the mineral and partly for the purpose of determining the character of the tourmaline from special localities, but none of them have been made for the special purpose of determining the chemical composition of the species. It seems sufficient to give the ratios only, which are as follows:

Locality.	Analyst.	SiO_2 :	B_2O_3 :	Total hydrogen.
69.†Mt. Bischoff	Sommerland	4 :	0·98 :	18·5
70. Campolongo	Engelmann	4 :	0·82 :	17·4
71. Sysersk, Urals	Cossa and Arzruni	4 :	0·89 :	18·8
72. Montgomery Co., Md.	Chatard	4 :	0·84 :	20·4
73. Nevada Co., Cal.	Melville	4 :	— :	20·8
74. Tamaya, Chili	Schwarz	4 :	1·02 :	19·1
75. Straschin, Bohemia	Weisner	4 :	1·10 :	19·4
76. Urulza, Siberia	Stchusseff	4 :	0·85 :	19·0
77. Kolar, India	Chapman Jones	4 :	0·87 :	19·1
	Average	4 :	0·92 :	19·2

* Bodewig, Zeitschr. für Kryst., viii, p. 211, 1883.

† 69, 70, 71 and 72 quoted in Dana's Mineralogy; 73, Bull. U. S. Geolog. Survey, No. 90, p. 39; 74, Zeitschr. deutsch. Geol. Gesell., xxxix, p. 238; 75, Min. u. Petr. Mitth., ix, p. 410; 76, Zeitschr. Kryst., xx, p. 93; 77, Min. Mag., xi, p. 61.

As indicated by the variations in the ratios, the analysts apparently have not had sufficient experience to enable them to deal successfully with such a difficult problem as the tourmaline analysis. The average of the ratios, however, approximates to 4 : 1 : 20 and thus substantiates our formula.

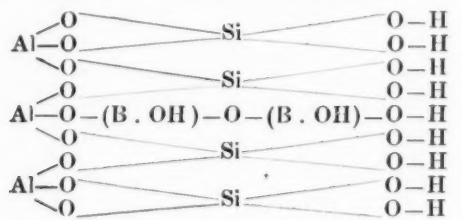
TITANIUM IN TOURMALINE.—Titanium seems to have been overlooked in the earlier analyses of tourmaline, but is reported in several of the analyses of Riggs, Jannasch and Kalb, and others. The quantity, however, has always been found to be small, amounting to over one per cent (reckoned as TiO_2) in only four of the analyses and to over 0·6 per cent in but two others. It has not been taken into consideration in making the foregoing calculations, partly because it would exert no appreciable influence on the final result, but chiefly because it is uncertain whether the titanium in this mineral plays the part of a tetravalent element replacing silicon, or of a trivalent element replacing aluminium. Although it may not be possible with the data now at hand to definitely settle this question, still the analyses furnish some evidence that the element should be regarded as trivalent. This result has been reached by considering titanium both as TiO_2 replacing SiO_2 and as Ti_2O_3 replacing Al_2O_3, and comparing the ratios derived from the four analyses in which the TiO_2 has been recorded as over one per cent. The results are as follows:

No.	Locality.	Premises.	SiO_2 : B_2O_3	Total hydrogen.
51.	Monroe, Conn., Riggs	TiO_2, 1·61 per cent	4 : 0·88	18·9
		Neglecting titanium	4 : 0·91	19·6
		Ti_2O_3 1·45 per cent	4 : 0·91	19·97
53.	Gouverneur, N. Y., Riggs	TiO_2 1·19 per cent	4 : 0·95	18·5
		Neglecting titanium	4 : 0·97	18·9
		Ti_2O_3 1·07 per cent	4 : 0·97	19.2
56.	Snarum, Jannasch and Kalb	TiO_2 1·10 per cent	4 : 0·93	19·1
		Neglecting titanium	4 : 0·96	19·7
		Ti_2O_3 0·99 per cent	4 : 0·96	19·9
59.	Tamatawe, Jannasch and Kalb	TiO_2 1·22 per cent	4 : 0·90	18·4
		Neglecting titanium	4 : 0·92	18·8
		Ti_2O_3 1·10 per cent	4 : 0·92	19·1

In these four cases it will be observed that the calculations give the closest approximation to the normal tourmaline ratio when the titanium is regarded as Ti_2O_3. Moreover when the titanium is regarded as TiO_2 the departure from the normal ratio is so great that it does not seem probable that this is due wholly to defects in the analyses. Some very careful and exact analytical work must be done in order to decide this question definitely.

CONSTITUTION OF TOURMALINE.—The evidence is convincing that all tourmalines are derivatives of a complex borosilicic acid $H_{20}B_2Si_4O_{21}$, and it is believed that further analyses will not alter this result, although they may furnish important data concerning the constitution of the acid. All of the hydrogen atoms of this acid in tourmaline are not replaced by metals, for the different varieties have always been found to contain water, which indicates the presence of hydroxyl. The ratio of the silica to the hydrogen derived from water (hydroxyl) plus the fluorine is not constant, but varies in Riggs' and our analyses from 4 : 3·14 (pale green tourmaline from Auburn, Maine) to 4 : 2·48 (colorless tourmaline from De Kalb). In all of the analyses in which water has been estimated directly, a sufficient quantity has been obtained to yield two hydroxyls in the formula; in only a few cases has the amount been sufficient to yield three hydroxyls. We are thus led to believe in the existence of two hydroxyls in all tourmalines, and it seems natural to associate them with the two boron atoms. The acid consequently becomes $H_{16}(B.OH)_2Si_4O_{19}$. The small amount of fluorine which is found in many varieties of tourmaline presumably plays the same role as hydroxyl, or is isomorphous with it, as in the case of topaz, of chondrodite, and of other minerals containing fluorine and hydroxyl. The slight excess of hydrogen over and above the two hydroxyls may be regarded as basic hydrogen, which plays the role of a metal. Such a relation is not unknown in complex mineral compounds.*

One of the peculiar features of tourmaline is that varying proportions of metals of different valences and of essentially different character replace the hydrogens of the acid $H_{16}(B.OH)_2Si_4O_{19}$. In all cases thus far examined aluminium predominates and is present in sufficient quantity to replace more than half the hydrogens. From this it has been inferred that an aluminium-borosilicic acid $H_9Al_3(B.OH)_2Si_4O_{19}$ *is characteristic for all varieties of tourmaline.* The constitution of this acid may be expressed graphically as follows:



* This Journal, xl, p. 396, 1890.

It would seem that the mass effect of the complex radical $[Al_3(B.OH)_2Si_4O_{19}]$, which has a valence of nine, is sufficiently pronounced to control or dominate all types of tourmaline. Thus it apparently makes no difference whether the nine hydrogens are replaced largely by aluminium and to a slight extent by alkalies; or largely by magnesium and to a slight extent by aluminium and alkalies; or to about an equal extent by aluminium, iron or magnesium and alkalies; the result in all cases is the mineral tourmaline, with its characteristic crystallization and its peculiar optical and electrical properties.

The following example (compare the ratio derived from the analysis of the green tourmaline from Haddam Neck, page 107) will illustrate the method of determining to what extent the nine hydrogens of the tourmaline acid, $H_9Al_3(B.OH)_2Si_4O_{19}$, are replaced by metals of different valences:

Ratio.	Total hydrogen equivalent, or 20 H.		2(OH, F).	18 H.	3 Al.	9 H.	
Al_2O_3		2·327		2·327	1·385	·942 ÷ ·154 = 6·1	R‴
FeO	·059						
MnO	·056	·169		·169		·169 ÷ ·154 = 1·1	R″
MgO	·008						
CaO	·046						
Na_2O	·068	·178		·178		·178 ÷ ·154 = 1·2	R′
Li_2O	·110						
H_2O	·344	·404	·308	·096		·096 ÷ ·154 = 0·6	H.
F	·060						
	20)3·078			2)2·770	9)1·385		9·0
	·154			1·385	·154		

From the ratio of the total hydrogen equivalent, $\frac{2}{20}$ (representing two hydroxyls) are deducted. The remainder, 18 H, is divided by two, thus determining the ratio of the nine H's replaced by Al_2 in the formula. The excess of the aluminium or trivalent metal ratio, R‴, together with the ratios of the bivalent metals, R″, the alkali metals R′ and the excess of hydrogen, H, represent nine H's, which are divided among the different constituents. Thus in the green tourmaline from Haddam Neck 6·1 hydrogens are replaced by Al (R‴), 1·1 by R″, 1·2 by R′ and there remains 0·6 excess of basic hydrogen.

The analyses of Riggs, Jannasch and Kalb, Scharizer and Chatard, given on page 555 of Dana's Mineralogy, together with our own analyses, practically include all varieties of tourmaline which have thus far been investigated, and in the following table are given the results of applying the foregoing method of calculation to them:

	No.	Locality.	Color.	Analyst.	R‴	R″	R′	H
Lithia Tourmalines.	1	Minas Geraes, Brazil	Pale-pink	Riggs, 37	6·7	0·3	1·2	0·8
	2	Rumford, Me.	Rose	Riggs, 36	6·5	0·2	1·2	1·1
	3	Brazil	Green	Jann. & Kalb, 64	6·3	1·1	0·9	0·7
	4	Auburn, Me.	Colorless	Riggs, 38	6·2	0·6	1·1	1·1
	5	Minas Geraes, Brazil	Pale-green	Riggs, 39	6·2	0·8	1·3	0·7
	6	Schüttenhofen, Bohemia	Red	Scharizer, 67	6·1	0·3	1·3	1·3
	7	Haddam Neck, Conn.	Pale-green	Authors	6·1	1·1	1·2	0·6
	8	Barra do Perahy, Brazil	Green	Jann. & Kalb, 63	6·0	1·1	1·4	0·5
	9	Rumford, Me.	Dark-green	Riggs, 42	6·0	1·3	1·1	0·6
	10	Minas Geraes, Brazil	Olive-green	Riggs, 41	5·9	1·1	1·3	0·7
	11	Auburn, Me	Light-green	Riggs, 40	5·7	0·9	1·2	1·2
	12	Schüttenhofen, Bohemia	Blue-green	Scharizer, 66	5·5	1·2	1·2	1·1
	13	Auburn, Me.	Dark-green	Riggs, 43	5·3	1·5	1·1	1·1
Iron Tourmalines, No. 21 excepted.	14	Buckworth, Australia	Black	Jann. & Kalb, 62	4·7	2·9	0·7	0·7
	15	Paris, Me.	Black	Riggs, 44	4·7	3·0	0·5	0·8
	16	Auburn, Me	Black	Riggs, 45	4·7	3·1	0·5	0·7
	17	Alabashka, Russia	Black	Jann. & Kalb, 57	4·7	3·2	0·5	0·6
	18	Mursinka, Russia	Black	Jann. & Kalb, 60	4·7	3·2	0·7	0·4
	19	Schüttenhofen, Bohemia	Blue-black	Scharizer, 65	4·5	3·0	0·5	1·0
	20	Piedra Blanca	Black	Jann. & Kalb, 58	4·4	3·2	0·6	0·8
	21	Montgomery Co, Md.	Green (*Cr*)	Chatard, 72	4·4	3·4	0·5	0·7
	22	Minas Geraes, Brazil	Black	Riggs, 46	4·3	3·5	0·5	0·7
Magnesia-Iron Tourmalines.	23	Stony Point, N. C.	Black	Riggs, 48	4·2	3·6	0·5	0·7
	24	Oláhpian	Black	Jann. & Kalb, 61	4·0	4·1	0·5	0·4
	25	Tamatawe	Black	Jann. & Kalb, 59	3·8	4·6	0·5	0·1
	26	Haddam, Conn.	Black	Riggs, 47	3·7	4·0	0·5	0·8
	27	Snarum, Norway	Black	Jann. & Kalb, 56	3·7	4·4	0·7	0·2
	28	Orford, N. H.	Dark-br'wn	Riggs, 52	3·6	4·1	0·6	0·7
	29	Monroe, Conn.	Dark-br'wn	Riggs, 51	3·4	4·1	0·7	0·8
	30	Nantic Gulf, Baffin's Ld.	Black	Riggs, 49	3·1	4·7	0·5	0·7
Magnesia Tourmal.	31	DeKalb, N. Y.	Colorless	Authors	2·5	5·7	0·3	0·5
	32	DeKalb, N. Y.	Colorless	Riggs, 54	2·2	5·7	0·4	0·7
	33	Gouverneur, N. Y.	Brown	Riggs, 53	2·2	5·6	0·4	0·8
	34	Hamburg, N. J.	Brown	Riggs, 55	2·0	6·2	0·2	0·6
Mg & Fe.	35	Pierrepont, N. Y.	Black	Riggs, 50	1·6	6·3	0·4	0·7

It will be observed that the extent to which the nine hydrogens of the acid $H_9Al_2(B.OH)_2Si_4O_{19}$ are replaced by metals, is very variable. The trivalent metal, R‴, is chiefly aluminium, and the extent to which the hydrogens are replaced by it ranges from 6·7 to 1·6. The bivalent metals represented by R″ are chiefly iron and magnesium, and the extent to which the hydrogens are replaced by them ranges from 0·2 to 6·3. In general R″ and R‴ are reciprocal. There is always some hydrogen replaced by the alkali metals R′, and some basic hydrogen. The results are arranged in the table according to a decrease in the replacement of the hydrogens by R‴, and according to this arrangement the different varieties of tourmaline fall into natural groups.

The first 13 examples are characterized by containing an appreciable quantity of lithium, while in the others none, or

not more than traces of this element have been found; these may therefore be designated as *Lithia Tourmalines*, which form a natural group. In this group R′ is higher than in other varieties, while H is somewhat higher than the general average; R‴ is very high and R″ correspondingly low. This variety of tourmaline has its particular mode of occurrence, being found in pegmatite veins associated with quartz, albite, microcline, orthoclase, muscovite and lepidolite. The material is generally delicately colored and often transparent and of gem-like quality. It is difficultly fusible when heated before the blowpipe, fusibility=5–5½.

At the opposite extreme, 31–34, are varieties which may be designated as *Magnesia Tourmalines*. In these R″, which is chiefly magnesium, is very high and R‴ correspondingly low, while R′ reaches its lowest limit, 0·2 to 0·4. These varieties are light-colored and at times of gem-like quality. They are easily fusible before the blowpipe, fusibility=3. With these No. 35 should be associated, for it differs only in containing considerable iron which is isomorphous with the magnesium, hence the color of this tourmaline is black. The last five are alike in their mode of occurrence. They have probably been formed in limestones containing magnesium by the contact action of intruded igneous masses during the pneumatolitic period, when such masses were giving off heated aqueous vapors containing boracic acid and fluorine compounds. They are found in coarse crystalline limestone, associated with graphite, phlogopite, pyroxene, amphibole, scapolite and apatite. Contact metamorphisms of this nature have recently been described by Lacroix.*

The intermediate varieties (Nos. 14 to 30) with the exception of No. 21 are black or dark brown, owing to the presence of iron. These are the ordinary tourmalines found in granites, gneisses and schists, and sometimes in pegmatite veins intimately associated with lithia tourmaline, as at Auburn and Paris, Maine. They too have probably resulted from the mineralizing action of heated aqueous vapors containing boracic acid and fluorine compounds, given off during the pneumatolitic period of cooling igneous rocks. A contact metamorphism of this character, attended by the formation of tourmaline vein stone, has been very carefully described by Hawes.†

Nos. 14 to 22 (No. 21 excepted) are characterized by containing iron and only a little magnesia, hence they may be designated as *Iron Tourmalines;* Nos. 23 to 30 contain both

* Le Granites des Pyrénées et ses Phenomènes de Contact, Bull. Carte Géologique de France, No. 64, Tome x, p. 54, 1898.

† The Albany Granite, New Hampshire, and its Contact Phenomena, this Journal, xxi, p 21, 1881.

magnesia and iron, and are hence designated as *Magnesia-Iron Tourmalines.* These two groups, however, grade into one another. The fusibility of these intermediate groups of tourmalines varies from 4·5 to 3, and decreases as the amount of iron and magnesia increase.

Although in this series of thirty-five analyses there are pronounced groups or types of tourmaline which may be recognized, nowhere in the series do the ratios of R‴, R″, R′ and H approximate so closely to rational numbers that a definite formula for any one type can be instituted. Riggs and Jannish and Kalb, however, have given special formulas for different types of tourmaline (pages 100 and 101) based upon multiples of the acid $H_{18}(B.OH)_2Si_4O_{19}$. Deducting from their formulas appropriate multiples of the aluminium-borosilicic radical $[Al_3(B.OH)_2Si_4O_{19}]$, it is found that the nine variable hydrogens of the tourmaline acid are replaced by metals of different valences in the following proportions:

		R‴	R″	R′	H
I. Lithia tourmaline	Riggs	7·0	0·0	1·3	0·7
	Jann. and Kalb	6·0	1·4	1·3	0·3
II. Iron tourmaline	Riggs	5·0	2·6	0·7	0·7
	Jann. and Kalb	5·0	3·0	0·7	0·3
III. Iron-magnesia tour.	Jann. and Kalb	4·0	4·0	0·7	0·3

Concerning the formulas for lithia tourmaline, Riggs' corresponds closely to No. 1, and Jannasch and Kalb's to Nos. 7, 8, 9 and 10 of our series (compare the table on p. 120), but neither of these complicated formulas furnishes a satisfactory expression for this type as a whole. Similar statements might be made concerning their formulas for iron tourmalines and for iron magnesia tourmalines. The endeavor to express the composition of tourmaline or of one of its types by a definite formula may be compared to the attempt to express the composition of the dark varieties of sphalerite by a formula. Thus $Zn_{11}Fe_4S_{16}$ would correspond to sphalerite, containing about 50·5 per cent of zinc and 15·7 per cent of iron, but zinc and iron are isomorphous and can mutually replace one another in sphalerite, and a variety containing less iron would have to be expressed by a different formula. When, however, we understand the isomorphous relations existing between zinc and iron, and express the composition by RS, where R=Zn and Fe, the composition becomes very much simplified.

In tourmaline we have an isomorphous relation of a very peculiar nature, for in the acid $H_9Al_3(B.OH)_2Si_4O_{19}$ the nine hydrogens may be replaced to a large extent either by the trivalent metal aluminium or by the bivalent metals magnesium

and iron without any decided change in crystalline form. This leads to the consideration of a certain phase of isomorphism which, as it seems to us, has not been considered with sufficient care, namely, the mass effect of complex radicals in influencing or controlling crystallization. Thus in their simple salts we do not regard sodium and potassium as isomorphous with calcium, but in some complex silicates, zeolites for example, we recognize Na_2 and K_2 as isomorphous with, or at least capable of replacing, calcium, barium and strontium. In some of the phosphates, dickinsonite and fillowite for example, we have sodium (Na_2) playing the same role as calcium, manganese and iron in replacing the hydrogens of phosphoric acid. In the garnet-sodalite group we have minerals with isometric crystallization, to which the following formulas have been assigned:*

$Ca_3Al_2(SiO_4)_3$	Grossularite	Garnet
$Fe_3Al_2(SiO_4)_3$	Almandite	Garnet
$(Cl-Al)Na_4Al_2(SiO_4)_3$	Sodalite	
$(NaSO_4-Al)Na_4Al_2(SiO_4)_3$	Noselite	
$(NaSO_4-Al)(Na_2, Ca)_4Al_2(SiO_4)_3$	Haüynite	
$(NaS_3-Al)Na_4Al_2(SiO_4)_3$	Lazurite	
$[(OH, F, Cl)_2.Al]_6Al_2(SiO_4)_3$	Zunyite	

When it is taken into consideration that isometric crystallization is exceptional in the group of silicates, we are led to believe that the sexivalent radical $[Al_2(SiO_4)_3]$, by virtue of its mass effect, controls or dominates the crystallization of these minerals. Not only are they isometric, but, with the exception of zunyite, which is tetrahedral, they all crystallize commonly in dodecahedrons. In sodalite, noselite and lazurite, such unlike constituents as chlorine, and the univalent sulphate and polysulphide radicals $(NaSO_4)'$ and $(NaS_3)'$ play the same part in the complex molecules. It is moreover probable that these unlike constituents are isomorphous in the sense that they can mutually replace one another, for Brögger and Bäckström have described homogeneous material containing the lazurite, haüynite and sodalite molecules, while appreciable quantities of chlorine are almost always found in noselite and haüynite, thus indicating the presence of the isomorphous sodalite molecule. It is to be expected that the larger and more complex the radical the more potent will be its mass effect in controlling or determining the crystal form. Thus in sodalite, noselite and haüynite the radical is very large, $[R'_4Al_2(SiO_4)_3]$, $R'_4 = Na_4$ or Ca_2.

Tourmaline, it would seem, furnishes an example somewhat analogous to that presented by the garnet-sodalite group. In

* Brögger and Bäckström, Zeitschr. für Kryst., xviii, p. 209, 1890.

this acid $H_9Al_3(B.OH)_2Si_4O_{19}$ the mass effect of the complex radical $[Al_3(B.OH)_2Si_4O_{19}]$ is so great, or, the role played by the replacement of the nine hydrogens is so subordinate, that the bivalent elements, Fe, Mg, Mn and Ca, and to a slight extent the alkalies, Li, Na and K, can replace aluminium as isomorphous constituents. This conclusion in some respects is analogous to that reached by Rammelsberg, who stated in 1870 that all tourmalines were derived from an acid H_6SiO_5, in which the six hydrogens were replaced in varying proportions by R'_6, R''_3, Al_2 and B_2. Applying Rammelsberg's idea to the acid $H_{18}(B.OH)_2Si_4O_{19}$, all varieties of tourmalines may be regarded as mixtures of the molecules

$R'_{18}(B.OH)_2Si_4O_{19}$, $R' = $Li, Na, K and H
$R''_9(B.OH)_2Si_4O_{19}$, $R'' = $Fe, Mg, Mn and Ca
$R'''_6(B.OH)_2Si_4O_{19}$, $R''' = $Al, Cr and small amounts of Fe and Ti.

It seems more logical and satisfactory, however, to consider all varieties of tourmalines as salts of the acid $H_9Al_3(B.OH)_2Si_4O_{19}$, in which the complex aluminium-borosilicic acid radical $[Al_3(B.OH)_2Si_4O_{19}]$ exerts a *mass effect* by virtue of which the remaining hydrogens may be replaced by metals of essentially different character without bringing about any pronounced change in crystalline form.

Note concerning the detection of ferrous and ferric iron in Silicates; by S. L. Penfield and H. W. Foote.

In the preliminary work connected with the study of the methods of the tourmaline analysis, considerable time was devoted to ferrous and ferric iron determinations. The ordinary method of dissolving in a mixture of hydrofluoric and sulphuric acids and titrating with potassium permanganate can not be applied readily to tourmaline because it is extremely difficult to dissolve the mineral. Riggs overcame this difficulty by using very fine powder and heating under pressure in a heavy platinum crucible provided with a lid which was held down by clamps. Jannasch and Kalb succeeded in decomposing the exceedingly fine, elutriated powder by heating in sealed glass tubes with a mixture of sulphuric and hydrofluoric acids, but the method was far from satisfactory. We have employed fusion with borax. In order to test the method, silicates containing varying proportions of ferrous and ferric iron were first carefully standardized by the method described by Pratt.* The powdered silicate and borax glass were then fused in a platinum boat in a combustion tube, through which a current of either nitrogen or carbon dioxide gas was conducted. These

* This Journal, xlviii, p. 149, 1894.

gases were first freed from all traces of oxygen by conducting them over a roll of heated bright copper gauze at one end of the tube. Decomposition is thus readily effected without any appreciable oxidation. After fusion the material can be dissolved in dilute sulphuric acid and titrated with potassium permanganate. With small quantities of iron the method gives very satisfactory results, but ferric iron suffers a slight reduction during fusion, hence the method can not be recommended as a quantitative one when accuracy is required. The amount of reduction is nearly proportional to the amount of ferric iron, and when about 6 per cent of Fe_2O_3 is present the error amounted to about 0·3 per cent. It is certain, however, that very satisfactory determinations of ferrous and ferric iron might be obtained by means of this method, by applying a correction which could be determined by experimenting with some artificial mixture of silicates containing approximately the same amount of ferric oxide as the mineral. It is difficult to understand the cause of this reduction, which was first noted by Rammelsberg,* and afterwards carefully studied by Suida.†

Fusion with borax furnishes, however, a most excellent means for decomposing insoluble silicates, when qualitative tests for ferrous and ferric iron are desired. The application of the method is as follows: The mineral and some borax glass are heated in a closed-tube over a Bunsen-burner flame until decomposition is complete, or nearly so. Water is then dropped upon the hot glass in order to crack it, and, when cold, the end of the tube is broken up and transferred to a test-tube. About 3^{cc} of dilute hydrochloric acid are then added, and the acid is boiled vigorously until the material is dissolved, when about 5^{cc} of cold water are added. The liquid, after being divided into two portions, may then be tested with potassium ferricyanide for ferrous iron, and with either ammonium thiocyanate or potassium ferrocyanide for ferric iron. The results are very satisfactory and decisive, and although there is a tendency for ferric iron to undergo slight reduction during fusion, and also a tendency for ferrous iron to undergo slight oxidation during the manipulation, these defects are so trifling that practically they may be disregarded.

Mineralogical-Petrographical Laboratory,
Sheffield Scientific School, January, 1899.

* Zeitschr. der deutsch. geolog. Gesell., xxiv, p. 69, 1872.
† Min. Mittheilung, Tschermak, 1876, p. 175.

ART. XIII.—*Littoral Mollusks from Cape Fairweather, Patagonia;* by HENRY A. PILSBRY. (With Plate I.)

IN the course of his paleontological explorations in Patagonia in the interest of Princeton University, Mr. J. B. Hatcher found time to make a small gathering of marine shells, at the locality named above. The scarcity of information upon the fauna of the east coast of South America makes it desirable to place the facts gained from even small collections on record, to the end that the limits of the faunal provinces of this coast may be more exactly defined, and their characteristics more fully exposed.

The fauna at the point in question is typically Magellanic, with but little admixture of types from the Argentine fauna of La Plata region. *Nacella*, *Photinula* and *Trophon*, *Plaxiphora* and littoral *Brachiopoda*, all occurring in a gathering so small as this, at once indicate the western and not northern origin of this mollusk population. *Bullia* alone is more northern in distribution, this being its most southern outpost.

The addition of the genus *Sphenia* to the Magellanic fauna is interesting and unexpected.

The figures on Plate I are three-fourths natural size.

MURICIDÆ.

Trophon Gerversianus Pallus.
Trophon Gerversianus Phillipianus Dkr.
Trophon fasciculatus Hombron and Jacquinot.
Trophon textiliosus Hombr. and Jacq. Pl. I, fig. 4.

Shell fusiform, white or slightly buff tinted, with moderately dilated body-whorl and short oblique or subvertical anterior channel. Whorls about 6, convex, separated by a deep suture, the last dilated toward the lip. Sculpture of numerous subregular rounded spiral cords (28–34 on body-whorl, 8–11 on penultimate whorl), separated by much narrower linear grooves, and numerous vertical folds, which are rather closely placed, separated by intervals narrower than themselves, are somewhat arcuate in harmony with the lines of growth and become obsolete upon the base. There are about 20 (18–21) folds upon the penultimate whorl, pretty regular and equal; but upon the latter part of the last whorl they become irregular or in part obsolete. Aperture ample, over half the total length of the shell, the outer lip somewhat expanding and faintly crenulated; columellar lip with a smooth white callous, reflexed over and closing the axial chink; siphonal fasciole well developed.

Alt. 36, diam. 23 mm.; alt. of aperture 22 mm.
" 39 " 21 " " " 21 "

The original description and figures were from a young shell. The species has not hitherto been recognized, probably owing to this circumstance. Mature specimens collected by Mr. Hatcher are here described and illustrated. The figures referred to *decolor* Phil. in the Voyage au Pol Sud. (Zool., pl. 25, f. 6–8), look like adults of *textiliosus*.

T. textiliosus has been reckoned a synonym of *T. Gerversianus* by Tryon (Man. Conch. II and III), but this is only another example of the "lumping" practised by him in dealing with *Trophon*.

It differs conspicuously from most other Cape Horn Trophons in its less rude sculpture and symmetrical contours. *T. decolor* Phil. has a much shorter anterior canal, purple interior and fewer spirals. In *T. cancellinus* Ph. the lip is thickened and dentate within. *T. crispus* Gld. differs in sculpture; and *T. liratus* Couth., which is apparently the most nearly allied species, has the anterior canal longer, and there are fewer spiral grooves. Specimens are in the collection of the Academy of Natural Sciences of Philadelphia from "Santa Cruz River, Patagonia, Wm. Bell."

BUCCINIDÆ.

Euthria plumbea Phil.

Enthria sp. undet. Like *plumbea*, but finely spirally striated throughout. All of the specimens are beach-worn and not suitable for description.

Bullia globulosa Kiener.

VOLUTIDÆ.

Scaphella Ferussaci Don.
Scaphella ancilla Sol.

CALYPÆTRIDÆ.

Trochita corrugata Reeve. Varies toward forms in which the radial ribs almost disappear.

TROCHIDÆ.

Photinula cœrulescens King.
Photinula tæniata Wood.

Photinula pruinosa Mab. and Roch. Quite distinct from the longer-known species in its Gibbula-like contour and wide, flattened, lusterless columella.

PATELLIDÆ.

Nacella ænea magellanica Gmel.
Nacella ænea deaurata Gmel.

MOPALIIDÆ.

Plaxiphora setigera King.

PECTENIDÆ.

Pecten patagonicus King.

MYIDÆ.

Sphenia Hatcheri n. sp. Pl. I, figs. 5, 6.

Shell cretaceous and dull, stout, rather strong, moderately inflated, with broad, somewhat truncated, closed anterior, and narrow, abruptly truncate and widely gaping posterior end. Beaks small, in close contact and eroded at the tips, nearly median, being one mm. nearer the posterior than the anterior end; projecting somewhat above. Dorsal margin highest anterior to the beaks, thence sloping downward and posteriorly; anterior end widely subtruncate, arcuate; ventral margin slightly arcuate. Sculpture, fine, nearly regular concentric grooves separating wider intervals on the anterior portion of shell, disappearing posteriorly, where there are only some rude, irregular wrinkles at unequal intervals. Face of the chondrophore in right valve directed ventrally; that of the left valve partially erect. Interior white or stained, porcellanous, the adductor scars distinct, pallial line and very broad posterior sinus indistinct. Length 17, altitude 9·5, diam. 7·2^{mm}. A single specimen collected. The genus has not before been reported from this region to my knowledge.

MACTRIDÆ.

Mactra (*Mactra* s. str.) *Jousseaumi* Mabille and Rochebrune. Pl. I, figs. 1, 2, 3.

The specimen figured, one of several collected, agrees with Mabille and Rochebrune's short and unsatisfactory description* as far as that goes, except in size; their specimen measuring, length 45, alt. 34, diam. 18^{mm}. The proportions however are similar, the figured specimen measuring 67, 48, 28^{mm}. The subtriangular form, perfectly straight slope of the valve margins in front of the beaks, and obtuse siphonal extremity, as well as the details of hinge structure, are sufficiently shown in the figure. In external texture it is like an old *Spisula solidissima*, but the thin, light yellowish-olive cuticle adheres in small ragged patches.

MYTILIDÆ.

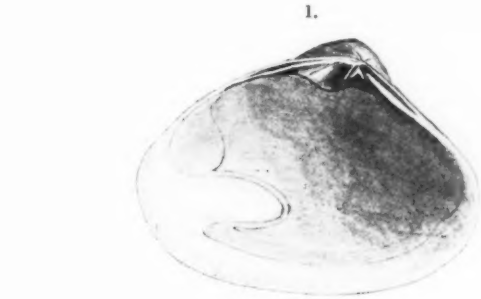
Mytilus magellanicus Gmel.
Mytilus sp. A single small specimen.
Mytilus edulis L.

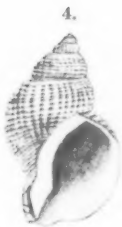
TEREBRATELLIDÆ.

Terebratella dorsata Gmel.

Academy of Natural Sciences, Philadelphia.

* Miss. Sci. du Cap Horn, Mollusques, p. 106.





LITTORAL MOLLUSKS FROM CAPE FAIRWEATHER, PATAGONIA.

ART. XIV.—*The Thermodynamic Relations for Steam;* by G. P. STARKWEATHER.

AMONG the various thermodynamic relations for a gas that between pressure, volume and temperature, the 'equation of condition' is one of the most important. To apply to the case of steam such equations, either empirical, or based on assumptions hardly justifiable, have been formed by Zeuner,* Schmidt,† Ritter,‡ and Antoine.§ Of these Zeuner's and Schmidt's satisfied the saturation line well, but they, as well as Antoine's, had the fatal defect that the constant which determines the limiting value of $\frac{pv}{T}$ for very great volumes was assumed incorrectly.

Van der Waals' celebrated pamphlet in 1873 gave a rational form to the equation of condition, and Clausius' generalization ‖ of the same,

$$p = \frac{RT}{v-a} - \frac{f(T)}{(v+\beta)^2},$$

has been for the most part adopted for various substances. Equations based upon this generally have the aim of satisfying not only the gaseous state but also the liquid. A relation between a and β, and also the value of $f(T)$ at the critical point, follow from the fact that at that point not only does this equation hold, but also its first and second partial derivatives with respect to v. R is fixed by the chemical composition of the substance, while $f(T)$ is so determined as to satisfy the corresponding saturation pressures and temperatures by Clausius' method.¶ The value of a (hence β, from the relation mentioned above) is so chosen as to satisfy the water line at some point.

The best application of this method to steam has been given by Van Laar,** who has taken for $f(T)$ the form adopted by Sarrau†† for carbonic acid, $\kappa\gamma^{-T}$, κ and γ being constants. On applying Clausius' method of determining the corresponding saturation pressures and temperatures to the equation he has found a good agreement.

* Zeitschr. des Ver. Deutsch. Ingen., xi, p. 42, 1867.
† Zeitschr. des Ver. Deutsch. Ingen., xi, pp. 649. 771, 1867, and Prag Abhandl., i, 1868.
‡ Wied. Ann., iii, p. 447, 1878.
§ Comptes Rendus, cx, p. 632, 1890.
‖ Wied. Ann, xiv, pp. 279, 692, 1881.
¶ Wied. Ann., xiv, p. 692, 1881.
** Zeitschr. für Phys. Chem., xi, p. 433, 1893.
†† Comptes Rendus, ci, pp. 941, 994, 1145, 1885.

But Van Laar's equation does not satisfy the saturation volumes. The writer has shown in a previous paper* that the saturation volumes as calculated from Regnault's latent heats are entirely out of accord with those directly measured by Battelli,† and has given reasons for preferring the former. From these Van Laar's equation deviates 2·5 per cent. Even should we assume Battelli's experiments to be correct instead of Regnault's the deviations would still exceed 1 per cent.

Were it certain that the equation were necessarily of Clausius' form, holding for the liquid as well as the vapor, the method would be exact, and we should simply have to say so much the worse for the experiments. But all we know concerning the last term of the second member is that at large volumes at any given temperature it must be sensibly $\frac{c}{v^2}$, as has been shown by Van der Waals. If we replace $\frac{1}{(v+\beta)^2}$ by some other function of v which is sensibly $\frac{1}{v^2}$ at large volumes, the application of Clausius' method becomes very complicated, if not, indeed, impossible. The failure of Van Laar's equation to satisfy the facts would seem to show that the form $\frac{f'(T)}{(v+\beta)^2}$ is not sufficiently correct for the water line, at least.

Abandoning the attempt to satisfy the water line throughout, we might still consider $\frac{f'(T)}{(v+\beta)^2}$ as sufficiently accurate for it in the vincinity of the critical point, the relations for that point still holding true. The equation would thus apply to steam for all states. In this case, if we give the equation Clausius' general form, his method for determining $f(T)$ does not apply, and we are free to choose it so as to satisfy the saturation volumes. This has apparently never been done. The writer has attempted it, but without success. $f(T)$ would necessarily decrease very rapidly with increasing temperature. Thus at 100° C., 200° C. and 365° C. (the critical temparature) $f(T)$ would have the respective values 59·5, 21·5 and 13·5. Moreover, the great fall from 100° to 200° is out of accord with the change from 200° to 365°. This seems to indicate that the type of formula selected will not satisfy the facts.

There remains the following problem, to obtain equations which shall satisfy the experiments within ordinary limits. Such equations would suffice for most purposes, and moreover the writer hopes to draw from them some theoretical conclu-

* This Journal, Jan. 1899, p. 13.
† Mem. R. Acc. Sc. di Torino (ii), 43, 1893.

sions of interest. A p-v-T equation should be of the form

$$p = \frac{RT}{v-a} - f(T)\phi(v).$$

In this R must have its theoretical value deduced from the chemical composition of water, while a, on account of the extreme incompressibility of water, should have a value not much less than 0·001, v being in cubic meters per kilogram. Moreover, $\phi(v)$ must be sensibly $\frac{c}{v^2}$ for large values of v.

The writer has formed the following equation, to hold for volumes not much less than 0·12 cubic meters per kilogram. At such volumes it should not be used when the pressure much exceeds 11700^{mm}, although for larger volumes it may be applied to higher pressures.

$$p = \frac{RT}{v-a} - \frac{A}{Tv^{\frac{3}{2}}(v^{\frac{1}{2}}+\gamma)}.$$

If p is expressed in millimeters and v in cubic meters per kilogram the constants are

log R = 0·539990	a = 0·0008
log A = 4·632127	γ = 1·20484

The value of R is that given by Van Laar,* modified by the fact that he places the absolute zero at −273°·2 instead of −273°·7, as assumed here.

How well the equation agrees with the saturation line is shown by the following table. In the first column is given the temperature absolute, in the second the pressure, p_C, calculated from the formula by means of the saturation volumes, in the third the pressure according to Regnault, p_R, and in the fourth the fractional deviation, d, of p_C from p_R.

T	p_C	p_R	d	T	p_C	p_R	d
313·7	55·11	54·91	+·0036	403·7	2026·4	2030·3	−·0019
323·7	92·37	91·98	+·0042	413·7	2712·2	2717·6	−·0020
333·7	149·34	148·79	+·0037	423·7	3573·3	3581·2	−·0022
343·7	233·66	233·08	+·0025	433·7	4641·7	4651·6	−·0021
353·7	355·04	354·62	+·0012	443·7	5950·9	5961·7	−·0018
363·7	525·64	525·39	+·0005	453·7	7538·1	7546·4	−·0011
373·7	760·01	760·00	0	463·7	9442·7	9442·7	0
383·7	1074·6	1075·4	−·0008	473·7	11700	11689	+·0009
393·7	1489·5	1491·3	−·0012				

With the exception of those near 323°·7 the variations are insignificant, but the change in sign at 463°·7 shows that the

* Zeitschr. für Phys. Chem., xi, p. 433, 1893.

equation will not hold for much smaller volumes. The larger deviations near 323°·7 are not due to the form chosen for the equation, for at such large volumes the gas deviates only slightly from the law of Boyle and Charles. A sufficient explanation for these deviations lies in the values of p and $\frac{dp}{dt}$, Regnault's formula for which is incorrect at low pressures, due to the fact that he did not recognize the sudden change in $\frac{dp}{dt}$ at 0°. This matter will be considered later.

p and T being given, the formula is not convenient for obtaining v, but if an approximate value of v be found from Boyle and Charles' law, p obtained, and then v corrected by the assumption

$$\delta \log p = -\delta \log v,$$

a second correction will generally be sufficient.

If the factor $\frac{1}{T}$ is correct, the term $v^{\frac{3}{2}}(v^{\frac{1}{2}}+\gamma)$ must be sensibly so, for it satisfies the volumes on the saturation line and approaches the value v^2 for large values of v. To justify the factor $\frac{1}{T}$ recourse would naturally be had to volumetric experiments on superheated steam. Since it has been shown in the previous paper, however, that such experiments do not appear reliable, a more roundabout method is necessitated to justify the factor.

We now proceed to obtain the equations for entropy, η, and energy, ϵ. The equations for energy formed by previous writers have all been based on the assumption that either the specific heat at constant pressure or that at constant volume is constant, or on another assumption equally unjustifiable, which will be mentioned later. There will be needed the quantity

$$\psi = \epsilon - T\eta,$$

and since

$$d\epsilon = Td\eta - pdv,$$

we have

$$d\psi = -\eta dT - pdv.$$

From this equation follow

$$\frac{\delta\psi}{\delta v}\Big]_T = -p \quad \text{and} \quad \frac{\delta\psi}{\delta T}\Big]_v = -\eta.$$

Substituting the value of p from our equation of condition in the first of these, and integrating, there results

$$\psi = -\mathrm{RT}\log_\varepsilon (v-a) - \frac{2\mathrm{A}}{\mathrm{T}\gamma v^{\frac{1}{2}}} + \frac{2\mathrm{A}}{\mathrm{T}\gamma^2}\log_\varepsilon \frac{v^{\frac{1}{2}}+\gamma}{v^{\frac{1}{2}}} + \mathrm{F(T)}$$

where F(T) is some unknown function of T. It should be observed that differences of ψ at constant temperature formed by means of this equation are more accurate than the value of p found by the equation of condition, for an integral cannot have a greater percentage of error than the integrand.

Making use of the equation

$$\eta = -\left.\frac{\delta\psi}{\delta \mathrm{T}}\right]_v$$

there is obtained

$$\eta = \mathrm{R}\log_\varepsilon (v-a) - \frac{2\mathrm{A}}{\gamma\mathrm{T}^2 v^{\frac{1}{2}}} + \frac{2\mathrm{A}}{\gamma^2\mathrm{T}^2}\log_\varepsilon \frac{v^{\frac{1}{2}}+\gamma}{v^{\frac{1}{2}}} - \mathrm{F'(T)}.$$

It is at once evident that here the factor $\frac{1}{\mathrm{T}}$ in the equation for p plays an important role, and this equation, together with the one to be obtained presently for the energy, may have a great error at small volumes, unless the factor $\frac{1}{\mathrm{T}}$ is justified.

From the equation

$$\epsilon = \psi + \mathrm{T}\eta$$

we find

$$\epsilon = -\frac{4\mathrm{A}}{\gamma\mathrm{T}v^{\frac{1}{2}}} + \frac{4\mathrm{A}}{\gamma^2\mathrm{T}}\log_\varepsilon \frac{v^{\frac{1}{2}}+\gamma}{v^{\frac{1}{2}}} + f(\mathrm{T})$$

where

$$f(\mathrm{T}) = \mathrm{F(T)} - \mathrm{T\,F'(T)}.$$

f(T), except for an additive constant, is the kinetic energy, or rather such part of it as depends on the temperature alone.

A number of writers have performed this same integration with their p-v-T equation, and have immediately assumed that f(T) is linear in the temperature. We are now in position to show that this assumption is contrary to the experimental data at hand by determining f(T) within certain limits. For, from the equation for ϵ, we have

$$f(\mathrm{T}) = \epsilon + \frac{a}{\mathrm{T}v^{\frac{1}{2}}} + \frac{b}{\mathrm{T}}\log_{10}\frac{v^{\frac{1}{2}}+\gamma}{v^{\frac{1}{2}}}$$

where, if ϵ is expressed in kilogrammeters and v in cubic meters per kilogram, the constants are given by

$$\log a = 6{\cdot}286713 \qquad \gamma = 1{\cdot}20484.$$
$$\log b = 6{\cdot}567998$$

Now ϵ and v are known on the saturation line for values of T from 273°·7 to 473°·7. For there

$$\epsilon = JH - p(v-w)$$

where H is the total heat, J the mechanical equivalent, and w the volume of water at the pressure and temperature under consideration. Consequently $f(T)$ is found for this range.

The values given for the energy on the saturation line by the last equation are untrustworthy at low temperatures, since there v is rather uncertain owing to the error in Regnault's formula for corresponding saturation pressures and temperatures. But from the equation for p, since for the region below 100° C. w is constantly 0·001, there is obtained

$$p(v-w) = \frac{RT(v-\cdot 001)}{v-\cdot 0008} - \frac{A(v-\cdot 001)}{Tv^{\frac{3}{2}}(v^{\frac{1}{2}}+\gamma)}.$$

In the first term of the second member, since v is large, any error in v cancels out. The last term is so small for the region where serious errors in v may occur that the volumes calculated from the latent heats may be used. This also is true concerning the values of the potential energy; any slight errors in the volumes at low temperatures will not affect things.

In this manner ϵ has been calculated for the saturation line, then $f(T)$, and the following table obtained. In the first column is given the absolute temperature, in the second the corresponding value of $f(T)$, and in the third, under $f'(T)$, the average rate of increase of $f(T)$ for each ten degrees.

T	$f(T)$	$f'(T)$	T	$f(T)$	$f'(T)$	T	$f(T)$	$f'(T)$
273·7	242870		343·7	252135		413·7	261362	
		141·5			126·4			146·6
283·7	244285		353·7	253399		423·7	262828	
		137·3			127·0			151·2
293·7	245658		363·7	254669		433·7	264340	
		133·4			127·1			155·7
303·7	246992		373·7	255940		443·7	265897	
		131·4			128·5			159·5
313·7	248306		383·7	257225		453·7	267492	
		128·7			133·4			163·3
323·7	249593		393·7	258559		463·7	269125	
		128·0			137·3			165·2
333·7	250873		403·7	259932		473·7	270777	
		126·2			143·0			

Leaving out the lowest temperatures, which will be considered presently, we have the very remarkable fact that $f'(T)$, instead of being constant, as is generally supposed, is an

increasing function of the temperature. Thiesen* in a recent paper has shown that the total energy, expressed as a function of v and T, is not linear in T, but it has never before been shown, so far as the present writer can discover, that the kinetic energy is not linear, although Massieu† has given a complicated proof that the specific heat at constant pressure increases with the temperature; this, indeed, was contemporaneously done by Weyrauch.‡ Regnault§ has found experimentally the same fact for carbonic acid gas.

This fact that $f'(T)$ is an increasing function of T is so important that it is well to speak of the proof more in detail. We have from page 133

$$f(T) = \epsilon_s - \pi_s$$

ϵ_s and π_s denoting respectively the values of the total and potential energies on the saturation line. At 100° C., 150° C. and 200° C. the values of ϵ_s are 254757, 259571 and 264336 respectively, and if the last number were increased by 49, ϵ_s would be linear in T. On the other hand the corresponding values of $-\pi_s$ are 1183, 3257 and 6441, the zero of potential energy being that of indefinitely rare gas, and the last exceeds a linear formula for π_s by 1110. Now it is impossible that by any change of p-v-T equation, hence a change of the form of π, the number 1110 can be reduced to 49.

We have next a remarkable corroboration of our formulæ, in particular of the factor $\frac{1}{T}$ in the last term of the p-v-T equation, by means of Regnault's experimental determination of the specific heat at constant pressure. At temperature 403°·7, pressure 760^{mm}, the volume is found by the p-v-T formula to be 1·8018 cubic meters per kilogram. We have then, if Q_1 is the quantity of heat necessary to turn one kilogram of water at 0° C. into this state at constant pressure,

$$\epsilon = JQ_1 - p(v-w) = JQ_1 - 18609.$$

But from the formula for ϵ on page 133, since we know (page 134) $f(403{\cdot}7) = 259932$, we have $\epsilon = 258909$, hence $JQ_1 = 277518$.

Similarly at temperature 473°·7, pressure 760^{mm}, we find the volume to be 2·1314. We thus obtain in the same way

$$JQ_2 = 292035,$$

Q_2 being the supply of heat necessary to turn one kilogram of water at 0° C. into steam of this second state, at constant pressure.

* Wied. Ann., 1897, No. 13, p. 329.
† Mem. des Savants Étrangers, vol. xxii, p. 58, 1876.
‡ Zeitschr. des Ver. Deutsch. Ing., xx, pp. 1, 71, 1876.
§ Mem. of the Institute of France, vol. xxvi, pp. 128, 129.

Accordingly, we find for the mean specific heat at atmospheric pressure from 403°·7 to 473°·7

$$C_p = \frac{Q_2 - Q_1}{473{\cdot}7 - 403{\cdot}7} = 0{\cdot}4846$$

or only 0·9 per cent greater than Regnault's mean specific heat at atmospheric pressure from about 401°·7 to 490°·7, namely 0·4805. When one considers that this deviation could be cancelled by a diminution of less than 0·05 per cent in the latent heat at 200° C., which is far within the limits of error, the essential corroboration of the formulæ is evident.

Gray * has attempted to show that Regnault's experiments on the specific heat of superheated steam give a value of 0·3787. He does this by comparing the total heat at 100° C. with the quantities of heat obtained in the experiments on superheated steam. But this is not allowable, as Regnault † himself distinctly states, and he would not even compare the heats in different series of experiments. In fact if the latter be compared some absurd results are obtained.

We have now to express $f(T)$ by a formula. To get as high a determination as possible the writer has taken Regnault's second determination of the mean specific heat at constant pressure, namely that from 138° C. to 226° C. at atmospheric pressure it is 0·48111. Assuming this to be true from 130° to 230°, we obtain the quantity of heat necessary to heat the steam at atmospheric pressure between those temperatures. Adding this to JQ_1 found on page 135 we obtain the quantity of heat necessary to heat water at atmospheric pressure from 0° C. into steam at 230° C., JQ_2. At the latter state the volume is 2·2713, so subtracting $p(2{\cdot}2703)$ from JQ_2 we find the energy at this state. From the energy formula $f(T)$ is found to be 275278.

It will be noticed that at low temperatures $f'''(T)$ apparently changes sign. This is entirely dependent on the formula chosen for total heats at those temperatures. In the preceding article, in forming the expression for the total heats from 0° C. to 100° C., it was assumed that since $\frac{d^2H}{dt^2}$ was negative above 100°, it was probably so below. Under this assumption we see $f''(T)$ to change sign. On the other hand, if we make $f''(T)$ of one sign throughout, namely positive, $\frac{d^2H}{dt^2}$ must change sign. Now it is far more probable that the latter does so, for it concerns only a particular set of states, namely those on the

* Phil. Mag., xiii, p. 337, 1882.

† Mem. of the Institute of France, vol. xxvi, pp. 165, 166.

saturation line, whereas $f''(T)$ refers to any states whatever. The writer has therefore assumed $f(T)$ to be represented in the range considered, so far as the accuracy of the experiments permits us, by the formula

$$f(T) = a + bT + cT^2$$

Determining a, b and c from the values of $f(T)$ at 273°·7, 373°·7 and 503°·7, there are obtained

$$a = 215126 \qquad \log b = 1{\cdot}902449 \qquad \log c = \bar{2}{\cdot}894845$$

How well $f(T)$ is represented by this formula is shown by the following set of values calculated from it, which should be compared with those given on page 134. In order to properly represent the inaccuracies of the formula, in the third column are given the fractional deviations in the latent heats which it would be necessary to assume in order to make the formula absolutely correct.

T	$f(T)$	d	T	$f(T)$	d	T	$f(T)$	d
273·7	242870	0	353·7	253200	−·0009	433·7	264536	+·0009
283·7	244107	−·0008	363·7	254562	−·0004	443·7	266023	+·0006
293·7	245358	−·0012	373·7	255940	0	453·7	267527	+·0002
303·7	246626	−·0015	383·7	257334	+·0005	463·7	269045	−·0004
313·7	247910	−·0017	393·7	258743	+·0008	473·7	270580	−·0010
323·7	249209	−·0016	403·7	260167	+·0011	503·7	275278	0
333·7	250524	−·0014	413·7	261608	+·0011			
343·7	251854	−·0013	423·7	263064	+·0011			

It will be noted that the negative deviations near 313·7 bring the latent heats nearer Griffiths' determinations. It is probable that the latent heats thus calculated from $f(T)$ as expressed by the formula are from 0° C. to 100° C. nearer the truth than those obtained from the formula for H given in the preceding article.

Theoretically it would be very gratifying if $f''(T)$, which is the specific heat at constant volume for very large volumes, should at low temperatures approach either $3R$ or $\frac{5}{2}R$. These are respectively 141·44 and 117·37. That the first is not approached is evident from the numbers on page 134. Whether or not the second is, is not conclusively shown; the total heats are not accurately enough known at low temperatures to determine this. Since $\frac{3}{2}$ R would be 165·01, it looks as though in the range say from −50° C. to +200° C. a change in the molecular deportment of the steam occurs, such that the number of degrees of freedom of the molecule increases, and the specific heat at constant volume changes from $\frac{5}{2}$ R to $\frac{7}{2}$ R. Such molecular change might explain why a difficulty exists in finding a p-v-T formula to satisfy both water and steam.

From the relation

$$f(T) = F(T) - TF'(T)$$

there follows

$$f'(T) = -TF''(T)$$

from which $F'(T)$ and $F(T)$ are determined. The formulæ for η and ψ on page 133 become accordingly

$$\eta = a' \log_{10}(v-\alpha) - \frac{b'}{T^2 v^{\frac{1}{2}}} + \frac{c'}{T^2} \log_{10} \frac{v^{\frac{1}{2}}+\gamma}{v^{\frac{1}{2}}} + d' \log_{10} T + e' T + K'$$

$$\psi = -a' T \log_{10}(v-\alpha) - \frac{b'}{T v^{\frac{1}{2}}} + \frac{c'}{T} \log_{10} \frac{v^{\frac{1}{2}}+\gamma}{v^{\frac{1}{2}}} -$$

$$d' T \log_{10} T - e'' T - \frac{e'}{2} T^2 + K''$$

where if η is in kilogrammeters per degree, ψ in kilogrammeters, and v in cubic meters per kilogram,

$\log a' = 2{\cdot}035657$	$\log b' = 5{\cdot}985683$
$\log c' = 6{\cdot}266968$	$\log d' = 2{\cdot}264662$
$\log e' = \bar{1}{\cdot}195875$	$\log e'' = 2{\cdot}050449$
$K' = 192{\cdot}2$	$K'' = 215126.$

These formulæ, with that for the energy, have the same limitations as to pressure and volume as the p-v-T formula, and in addition can be used only when T is not far above 503°·7 or far below 273°·7.

The value of K′ was determined so as to make the entropy correct for the saturation line at 373°·7; the remaining quantities follow from others previously determined. How well the formula for η represents the saturation line is shown by the following table, in the third column of which are given the fractional changes in the latent heats necessary to make the formula for η correct. These should be the same as those given on page 137, but there are differences, very slight, however.

T	η	d	T	η	d	T	η	d
273·7	935·4	+·0011	343·7	788·2	−·0011	413·7	702·5	+·0010
283·7	908·5	0	353·7	773·1	−·0010	423·7	693·3	+·0011
293·7	883·9	−·0007	363·7	759·2	−·0006	433·7	684·4	+·0008
303·7	861·4	−·0011	373·7	746·3	0	443·7	676·3	+·0008
313·7	840·7	−·0015	383·7	734·2	+·0005	453·7	668·5	+·0002
323·7	821·7	−·0015	393·7	722·9	+·0005	463·7	661·3	−·0002
333·7	804·3	−·0013	403·7	712·4	+·0009	473·7	654·5	−·0005

It has been remarked that Regnault's formula for corresponding pressures and temperatures is incorrect at low temperatures. Also Wiebe * has taken exception to his determinations near

* Zeitschr. für Instrumentenk., xiii, p. 329, 1893.

80° C. There will now be developed a formula for p from the latent heats.

We have from Clausius for the saturation line

$$v - w = \frac{\mathrm{JL}}{\mathrm{T}} \frac{d\mathrm{T}}{dp},$$

from which follows

$$\frac{dp}{pd\mathrm{T}} = \frac{d \log p}{d\mathrm{T}} = \frac{\mathrm{JL}}{\mathrm{T}p\,(v-w)}.$$

Let us denote this by D. We have already obtained $p\,(v-w)$ with great accuracy (page 134) for temperatures below 100° C. For L we take the values from the assumed equation for $f(\mathrm{T})$, which seem to be the best obtainable. Thus D is found for various values of T.

Next the writer has assumed that D is represented by

$$\mathrm{D} = \frac{\mathrm{A}}{\mathrm{T}^2} + \frac{\mathrm{B}}{\mathrm{T}^3} - \frac{\mathrm{C}}{\mathrm{T}^4}.$$

This is Rankine's form, with the addition of the term $\frac{\mathrm{C}}{\mathrm{T}^4}$.

Determining A, B and C from the values of D at 273°·7, 323°·7 and 373°·7, there are found

$$\log \mathrm{A} = 3{\cdot}539061 \qquad \log \mathrm{B} = 5{\cdot}826374 \qquad \log \mathrm{C} = 7{\cdot}556878$$

How well this represents D is shown by the following comparison. Under D is given the value as first found from the latent heats, and under D′ that according to the formula.

T	D	D′	T	D	D′
273·7	0·0724625	0·0724626	333·7	0·0462057	0·0462064
283·7	0·0667980	0·0667857	343·7	0·0432180	0·0432188
293·7	0·0617441	0·0617298	353·7	0·0405067	0·0405049
303·7	0·0572187	0·0572100	363·7	0·0380399	0·0380322
313·7	0·0531516	0·0531546	373·7	0·0357738	0·0357738
323·7	0·0495038	0·0495037			

Integrating, there is obtained

$$\log_{10} p = -\frac{\mathrm{A}'}{\mathrm{T}} - \frac{\mathrm{B}'}{\mathrm{T}^2} + \frac{\mathrm{C}'}{\mathrm{T}^3} + \mathrm{K}$$

where

$$\log \mathrm{A}' = 3{\cdot}176848 \qquad \log \mathrm{B}' = 5{\cdot}163131$$
$$\log \mathrm{C}' = 6{\cdot}717544 \qquad \mathrm{K} = 7{\cdot}844259$$

K is determined by making p equal to 760^{mm} when T is 373°·7. In the following table the values of p according to this formula are given in the second column, in the third are Regnault's

pressures, p_R, in the fourth the fractional deviations of the former from the latter, and in the fifth a few determinations at low temperatures recently made by Juhlin.*

T	p	p_R	d	p_J
273·7	4·626	4·6	·006	4·618
283·7	9·277	9·165	·012	9·242
293·7	17·632	17·391	·014	17·46
303·7	31·943	31·548	·013	
313·7	55·449	54·906	·008	
323·7	92·610	91·980	·007	
333·7	149·40	148·79	·006	
343·7	233·59	233·08	·005	
353·7	354·94	354·62	·003	
363·7	525·56	525·39	·0003	
373 7	760	760	0	

The variations are considerable, but for those at low temperatures an explanation has already been given, and in the middle of the scale they are not more than could be ascribed to Regnault's not correcting his thermometer to the air-thermometer. Above 100° C. Regnault's gives two formulas, one for temperatures according to the air-thermometer, the other for temperatures by his mercurial thermometer; below 100° this is not done, the inference being that corrections were not made. Now Regnault remarks† that at about 50° C. the air-thermometer differs from the mercurial by two-tenths of a degree, which would be sufficient to account for the deviations in that region. The pressures are on the same side of Regnault's as those of Juhlin, and agree well from 80° to 100° with those of Wiebe.

In the following table are given values of various quantities for the saturation line from 0° C. to 100° C. on the basis of the formulæ developed in this paper, and from 100° to 200° from the formulæ adopted in the preceding article. They represent, in the writer's opinion, the best determinations possible with the data at hand. In the first column is given the temperature Centigrade, in the second the heat of the liquid, in the third the total heat, in the fourth the latent heat, in the fifth the pressure, in the sixth the volume, in the seventh the entropy of water, η_w, and in the eighth and ninth the entropy and energy of dry saturated steam, η_s and ϵ_s.

* Beiblaetter zu Wied. Ann., xviii, p. 736.
† Comptes Rendus, lxix, p. 884, 1869.

t	h	H	L	p	v	η_w	η_s	ϵ_s
0	0	598·9	598·9	4·626	204·97	0	935·4	242851
10	10·0	602·8	592·8	9·277	105·91	15·5	908 5	244072
20	20·0	606·8	586 8	17·632	57·653	30 3	883·9	245297
30	30·0	610·7	580·7	31·943	32·861	44·5	861·4	246524
40	40·0	614·6	574·6	55·449	19·518	58·4	840·7	247749
50	50·0	618·5	568·5	92·610	12·032	71·7	821·7	248966
60	60·0	622·3	562·3	149·40	7·6666	84·7	804·3	250168
70	70·0	626·0	556·0	233·59	5·0333	97·3	788·2	251353
80	80·1	629·7	549·6	354·94	3·3953	109·7	773·1	252515
90	90·2	633·3	543·1	525·56	2·3472	121·7	759·2	253652
100	100·4	636·7	536·3	760	1·6587	133·5	746·3	254757
110	110·5	639·8	529·3	1075·4	1·1973	144·9	733·9	255724
120	120·6	642·9	522·3	1491·3	0·88099	156·1	722·6	256691
130	130·7	645·9	515·2	2030·3	0 65948	167·0	711·9	257649
140	140·9	648·9	508·0	2717·6	0·50152	177·6	702·0	258615
150	151·1	651·9	500·8	3581·2	0·38707	188·0	692·7	259571
160	161·3	654·8	493·5	4651·6	0 30278	198·1	684·0	260517
170	171·6	657·7	486·1	5961·7	0·23982	208·1	675·9	261485
180	181·9	660·5	478 6	7546·4	0·19216	217 9	668·4	262440
190	192·2	663 3	471·1	9442·7	0·15566	227·5	661·4	263394
200	202·5	666·0	463·5	11689	0·12739	236 9	654·7	264336

The unit here for quantities of heat is the specific heat at 15°, pressures are in millimeters of mercury, volumes in cubic meters per kilogram, energy in kilogrammeters (at Paris) per kilogram, and entropy in kilogrammeters per kilogram per degree.

There is a gratifying confirmation of the formulæ given by Dieterici's experimental determination* of the volume at 0° C., which was 204·68 cubic meters. This differs from the value given in the table by only a little over one-tenth of one per cent. When one considers the roundabout way in which the latter was found, the agreement is quite remarkable. Dieterici considers his determination to be correct within one-half of one per cent.

There are one or two interesting points which can be brought forward concerning the deportment of steam over ice. At 0° C. that portion of the energy due to the terms in the formula containing v is only nineteen kilogrammeters, which is entirely negligible compared with the latent heat. Hence for steam over ice we can set

$$\epsilon = f(\mathrm{T}).$$

Now if G is the latent heat of ice, and K its specific heat, we have

$$\epsilon = \mathrm{JL} - \mathrm{JK}\,(273{\cdot}7 - \mathrm{T}) - \mathrm{JG} - p\,(v - w).$$

Hence

$$\mathrm{JL} - \mathrm{JK}(273{\cdot}7 - \mathrm{T}) - \mathrm{JG} - p\,(v - w) - f(\mathrm{T}) = 0.$$

* Wied. Ann., xxxviii, p. 1, 1889.

Below 273°·7 we can set

$$pv = p(v-w) = \mathrm{RT}.$$

Then, since

$$\mathrm{JL} = \mathrm{T}(v-w)\frac{dp}{d\mathrm{T}} = \frac{\mathrm{T}p(v-w)}{p}\frac{dp}{d\mathrm{T}} = \mathrm{RT}^2\frac{d\log p}{d\mathrm{T}}$$

we have

$$\mathrm{RT}^2\frac{d\log p}{d\mathrm{T}} - \mathrm{JK}(273{\cdot}7-\mathrm{T}) - \mathrm{JG} - \mathrm{RT} - f(\mathrm{T}) = 0$$

Now first suppose that determinations of L below 0° C. are made, or that those above 0° C. are so accurate that an expression for $f(\mathrm{T})$ is obtained for that region which will bear extrapolation below 0° C. Then $\frac{d\log p}{d\mathrm{T}}$ is known and a relation between p and T determined. Conversely, if the relation between p and T below 0° C. is known, $f(\mathrm{T})$ is at once determined, and thence the latent heats.

ART. XV. — *Descriptions of imperfectly known and new Actinians, with critical notes on other species*, III; by A. E. VERRILL. *Brief Contributions to Zoology from the Museum of Yale College*, No. LX.

Family PARACTIDÆ Hertwig, op. cit., 1882. Andres, op. cit., p. 255, 1884. McMurrich, Proc. U. S. Nat. Mus., xvi, p. 160, Jl., 1893.

Paractidæ + Sideractidæ Daniel., 1890.
Paractidæ + Actinostolidæ Carlgren, Kongl. Svenska. Akad. Handl., xxv, II, pp. 64, 137, 1893.

Entacmæous actinaria provided with a mesodermal sphincter muscle, but destitute of acontia. Mesenteries usually numerous, nearly always with 12 or more pairs perfect, the number and arrangement not always truly hexamerous. The perfect and larger imperfect mesenteries are usually fertile. Column-wall is usually smooth, sometimes with submarginal plications and solid ridges; rarely with low wart-like elevations or small verrucæ, sometimes capable of attaching sand, etc. No actinobranchs. No acrorhagi. No disk-tubercles.

The mesoglœa of the wall is usually tough and elastic, thin or thick, often parchment-like or subfibrous, in deep sea forms often thick and coriaceous. Base with an adhesive disk, which is sometimes amplexicaul, embracing permanently the stems of gorgoniæ, etc. Mouth with two siphonoglyphs and numerous lateral folds. Tentacles simple, usually numerous and retractile. Margin generally capable of involution.

This family appears likely to become an extensive one when all the species, whose places in the system are still doubtful, shall have been studied anatomically. At present there is no practical and sure way to distinguish the *Sagartiadæ* from this family except by the presence of *acontia* in the latter, and this is not always a satisfactory test* with preserved specimens. However, the thin, smooth, tough, wall is often a fairly good indication of this family, as is also the large number of perfect

* All the acontia may be ejected and lost by violent contractions, when certain *Sagartiæ* are placed in preservatives, or they may be easily decomposed in poorly preserved specimens. So they are often not to be found in specimens known to have had them in life. On this account it is doubtful whether several of the genera described by Danielssen, 1890, as destitute of *acontia*, belong to *Paractidæ* or *Sagartiadæ*. Of these *Stelidiactis*, *Altantactis*, *Anthosactis*, *Kyathactis*, and *Korenia* are described as having pores or cinclides in the wall (the last has them also in the disk). These genera may, therefore, be sagartians that have lost their acontia. The first three have only 6 pairs of perfect and sterile mesenteries, as is often the case in *Sagartiadæ*; the fourth has 20 perfect pairs; the last has 24 perfect pairs; the base is amplexicaul. His *Sideractis* is octamerous, with 16 perfect pairs of very thin mesenteries, partly fertile; tentacles not retractile, 8 inner ones large; sphincter mesodermal. It probably belongs with *Paractidæ*.

and fertile mesenteries, which are usually thin and have feeble and diffuse longitudinal muscles.

This family now appears to include *Paractis*, *Stomphia*, *Actinostola*, *Actinernus*, *Actinolobopsis*,* *Pycnanthus*, *? Sideractis*, *Cymbactis* (near *Stomphia*), *Tealidium*, *Paranthus*, *? Paractinia*, *Kadosactis*, *Phelliopsis*,† nov. (type *P. Panamensis* V. '69), *Alloactis*, nov. (type *A.*, *excavata* Hert.), *Raphactis*, nov., *Synanthus* Ver., *Ammophilactis*, nov. (type *A.*, *rapiformis* Les.).

The last named genus is remarkable for its small base and for having minute adhesive suckers near the margin. It agrees with *Paranthus* in living buried in sand and in its elongated form.

Raphactis, gen. nov. Type *R. nitida* V.

Paractidæ having a short column, with thin wall and submarginal longitudinal plications, with raised folds or solid ridges of mesogloea. Sphincter muscle enlarged distally in a thickened portion of the wall, above which the thin wall can be involuted; below this fold the wall may be smooth, or wrinkled, or slightly warty, but without suckers.

Base either broadly expanded, with thin edges, or amplexicaul and embracing permanently stems of gorgoniæ, etc., and in this case the opposite edges of the same or of different individuals unite by sutures.

Tentacles numerous, rather stout, in several rows, retractile. Mesenteries numerous, 12 or more pairs perfect and fertile; some imperfect ones may also be fertile. Stomodæum short. This genus lacks the pores of the disk and wall described in *Korenia*. *Synanthus* Ver. is closely allied in form and habit; it has a smooth wall and only six pairs of perfect, but fertile, mesenteries.

Raphactis nitida, sp. nov. Figures 18, 22.

Base large, either broadly expanded, with thin edges, or else clasping stems of sponges, hydroids, etc., and in the latter case the opposite lobes may unite together in a close suture; it secretes a tough thin cuticle. Column in contraction low and broad, most of its surface smooth and white in alcohol, often somewhat glossy or, in others, with a parchment-like appearance. The infolded summit is strongly plicated. Toward the contracted summit there is a much thickened fold, usually covered with a series of unequal longitudinally convergent, low, rounded, solid ridges, which vary in number and size, and are

*This new name is proposed for *Actinoloba* Hert., 1882 (*non* Blainv., 1834.) The type is *A. reticulata* (Dana, sp.) of Patagonia, etc.

† This name is proposed for those species of paractids that have been described as *Phellia*, on account of the adherent cuticle. They have usually 12 or more pairs of perfect, fertile, and very muscular mesenteries.

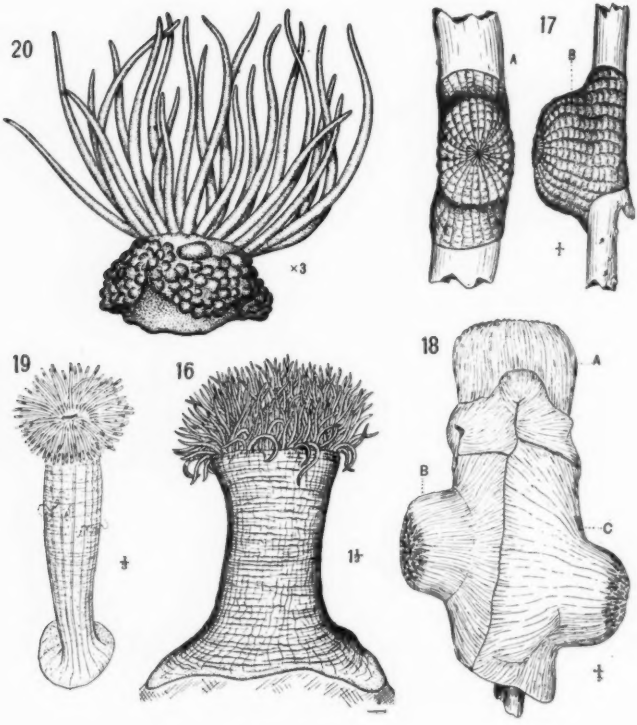
often lacking or concealed in the smaller examples; in the larger ones about 24 longer, alternating with shorter. Tentacles of moderate size, thick, tapered, blunt, crowded in five or six rows; in the larger specimens sometimes more than 144 in number; the inner are much longer and stouter than the outer ones. The walls of the tentacles are thick, and uniform. In section the column-wall is generally thin, but tough; toward the collar it becomes gradually much thickened and very firm. Sphincter muscle mesoglœal, imbedded in the thick collar, large, diffuse, club-shaped distally. Mouth large, with two broad shallow siphonoglyphs and about 12 to 14 distinct folds on each side. The siphonoglyphs may lie in the direction of the short axis of the body, or the reverse. Mesenteries regularly hexamerous, in more than four cycles, the fifth usually more or less incomplete; 12 pairs are perfect and fertile and in the larger specimens 16 pairs may join the stomodæum near its upper end; many of the smaller imperfect ones of the fourth cycle are also fertile; those of the fifth cycle are very small except close to the disk and basal membranes where they become larger and some bear small gonads close to the disk. No acontia were found. The stomodæum is very short and broad, strongly plicated within. The gonads are small; those of the perfect mesenteries are close to the base. Septal foramina of large size occur at about mid-height of the column. Diameter of column of the larger examples, contracted in alcohol, ·85 inch (20–22^{mm}); of base 1·5 inch (36^{mm}); height of column ·75 inch (18^{mm}).

Color in life was not noted.

Station 1043, U. S. Fish Com., Str. Albatross, in 130 fathoms off E. coast U. States, latitude of Delaware Bay.

This species has the habit common to many genera and species of deep-sea *Paractidæ* and *Sagartiadæ* of clasping with its base the stalks of hydroids, gorgoniæ, sponges, etc. When the opposite lobes come in contact they unite in a suture.* So, likewise, do the edges of the bases of adjacent individuals, as shown in fig. 18, A, B, C, and fig. 22.

* Hertwig made this habit a generic and family character, in the case of *Amphianthus* and *Stephanactis*, giving it, undoubtedly, an exaggerated importance, for the same species may live either in this way or attached by a broad base to a shell or stone, as I have repeatedly observed in *Actinauge Verrillii* McMur. (= *nodosa* Ver.) and other species. It is even doubtful whether it should be of generic value in any case. *Stephanactis* was used by me in 1868 for a genus near *Discosoma*, consequently I propose for the group thus named by Hertwig the new name *Stephanauge*. It is near *Actinauge* and *Hormathia*. The type, *Stephanauge abyssicola* (Moseley, 1877) is identical with my *Actinauge nexilis* (1883) and came from the same region. *S tuberculata* (Hert.) is very similar, if not the same, but it came from the Pacific Ocean, as did *S. hyalonematis* (McMur., 1883), which last is very imperfectly known The structure of this genus will be discussed later It differs from *Actinauge* chiefly in having the thick wall smooth below the fold, and perforated by distinct cinclides.



Explanation of cuts.

FIG. 16. *Paractis nivea* (Less.). Peru. × 1½.
FIG. 17. *Raphactis Caribæa* Ver. on a gorgonian, nat. size, front and side view, contracted. West Indies, 124 fathoms.
FIG. 18. *Raphactis nitida* Ver., three examples. A, B, C, natural size, united together by sutures; contracted in alcohol.
FIG. 19. *Sagartia (Psammactis) modesta* Ver., ½ nat. size, from life, New Haven.
FIG. 20. *Viatrix globulifera* D. and M., 1860. × 3. Bermuda.
All the drawings are by A. H. Verrill.

Erratum—In No. II of this series, p. 42, I erroneously referred *Actinia cruentata* Dana to *Bunodactis*, overlooking the anatomical description of McMurrich (Proc. U. S. Nat. Mus., xvi, p. 150, 1893), under the name *Condylactis cruentata*. It should, I now believe, be called *Actinoides cruentata*, as it agrees closely with the typical species of the latter genus. Page 45, *Bunodella stelloides*. Since the publication of No. II, I have received from Mr. J. E. Duerden, of Jamaica, larger examples of this species. On dissection they were found to have 24 pairs of perfect and fertile mesenteries, thus agreeing with *Bunodactis*. The genus *Bunodella* must, therefore, be dropped, and this species be called *Bunodactis stelloides*. Moreover the name *Bunodella* had already been used by Matthews for a genus of *Eurypteroidea*.

Art. XVI.—*A Volumetric Method for the Estimation of Boric Acid;* by Louis Cleveland Jones.

[Contributions from the Kent Chemical Laboratory of Yale University—LXXVIII.]

When boric acid and mannite are mixed in solution, a peculiar compound of strongly acid properties is the result. This compound decomposes carbonates, and its acid taste is comparable to that of citric acid, much stronger than that of boric acid alone. Magnanini* has found that the product of such a mixture of boric acid and mannite solutions shows greater electrical conductivity and a lower freezing point than a similar molecular solution of either substance alone. Other polyatomic alcohols (but all to a less degree than mannite) and some organic acids show this peculiar property of combining chemically with boric acid to increase its acid qualities.† Of this reaction between boric acid and the polyatomic alcohols, Thomson,‡ Barthe,§ and Jörgensen‖ have taken advantage to develop methods for the volumetric estimation of boric acid. Glycerine is used to form a combination with boric acid, sufficiently acidic to give an acid reaction when used with a sensitive indicator and make possible its titration with an alkaline solution. Hönig and Spitz¶ show that in the method of Jörgensen a very large amount of glycerine must be used to prevent the appearance of the indication of alkalinity with phenolphthalein before all the boric acid is neutralized according to the following equation: $2NaOH+B_2O_3=2NaOBO+H_2O$—; that in the presence of carbonates the solution must be boiled to decompose bicarbonates and the escape of boric acid by volatilization prevented by the use of a return condenser, and that silica must be removed by the process of Berzelius, and the solution then neutralized by the use of methylorange before a titration of the boric acid can be made.

Vadam,** for the estimation of boric acid in butter, makes use of mannite, which, as he finds, gives sharper indication with litmus than glycerine. According to this process, the solution to be analyzed for boric acid is neutralized by the use of litmus and a solution of sodium hydroxide. Mannite (1–2 grm.) is then added, bringing about an acid reaction with the boric acid present in free condition. The solution is then titrated to alkalinity by sodium hydroxide.

* Gaz. Chim., xx, 428–440, xxi, 134–145.
† Klein, J. Pharm. Chim., 4, vol. xxviii; Lambert, Comp. Rend., cviii, 1016–1017.
‡ J. S. C. I., xv, 432. § J. Pharm. Chim., xxix, 163.
‖ Zeitschr. f. Angew. Chem., 1897, 5.
¶ Zeitschr. f. Angew. Chem. (1896), 549.
** J. Pharm. Chim (6), viii, 109–111.

None of the above methods with glycerine have, in my experience, given anything but comparatively crude results. The weak acidic properties of boric acid, the interference (and difficulty of removal) of carbondioxide with all organic indicators sufficiently delicate to be used with boric acid, and indeed, the procuring of a standard alkali containing no carbonate, together with the supposed detrimental influence of silica and the lack of a convenient method for its removal, have made the process of Gooch,* which involves distillation and weighing with calcium oxide, the only means (though requiring long time and exceeding care) in use for the accurate separation and estimation of boric acid. Recently sodium tungstate has been recommended from this laboratory† as a substitute for calcium oxide to retain the distilled boric acid. The entire process, however, is one of the most exacting in analytical chemistry, and for this reason a convenient, rapid and at the same time accurate method for the estimation of boron is especially desirable. The first step toward the development of such a process must be the convenient preparation and the accurate estimation of the standard solution of alkali to be used for neutralizing the boric acid. This has been found to be easily accomplished by the process recommended by Küsler.‡ This observer, in an extensive investigation of the analytical methods for the volumetric estimation of alkalic and alkali carbonates in solution, finds that both phenolphthalein and methylorange are appreciably sensitive to carbonic acid, but when this interfering agent is removed by precipitation with barium chloride according to the process of Winkler,§ the remaining free alkali may be estimated with great accuracy by phenolphthalein and decinormal hydrochloric acid.

Obviously, if the difficulties dependent upon the action of carbon dioxide can be obviated, and if the acidity of the boric acid can be increased to such an extent that a sufficiently sensitive indicator will give with accuracy the neutralization point with free alkali, and if the alkali and stronger acid can be combined while boric acid alone remains free, then it should be possible to estimate boric acid volumetrically. Experiment has shown that barium chloride removes carbon dioxide, and that mannite makes a combination with boric acid strongly acidic to phenolphthalein.

* Amer. Chem. Jour., ix, 23–33: Moissan, Comp. Rend., cxvi, 1087: Kraut, Zeitschr. f. Anal. Chem., xxxvi, 165; Montemartini, Gaz. Chim. Ital., xxviii, I, 344.

† Gooch and Jones, this Journal, vii, 34.

‡ Zeitschr. f. Anorg. Chem., xiii, 124–150.

§ Massanalyse.

To obtain the boric acid alone in free condition many attempts have been made. Gladding,* Thaddeeff† and Rosenbladt‡ have isolated the boric acid by distillation with methyl-alcohol and a non-volatile acid. Many indicators theoretically insensible to free boric acid have been used to indicate the neutralization of the stronger acids. Hönig and Spitz,§ and Thomson,‖ use methylorange, Morse and Burton,¶ tropaeolin 00, while Vadam** makes use of litmus. All these indicators, however, have been found by experiment to be more or less affected by boric acid in solution. On the other hand, I have found in the well-known reaction according to which a stronger acid liberates regularly iodine from a mixture of iodide and iodate, the solution of this difficulty. If both the iodide and iodate are in excess of the acid the entire amount of free acid will be neutralized and the corresponding amount of iodine liberated according to the following equation:

$$5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2.$$

This liberated iodine may be removed by sodium thiosulphate and a solution obtained which is absolutely neutral containing only neutral salts, potassium iodide, iodate and tetrathionate. The statements made by P. Georgevic†† and Furry,‡‡ that boric acid present in moderate amount in solution has not the slightest action on a mixture of iodide and iodate, have been experimentally verified. Therefore when this acid is liberated by an excess of a stronger acid, and the iodine set free destroyed by thiosulphate, it remains free in solution to be titrated in any convenient manner possible.

Following along the lines suggested by the above reactions, a volumetric process for the estimation of boric acid has been developed. For a basis of the investigations, a standard solution of boric acid was prepared by dissolving in a liter of water about eight grm. of carefully weighed anhydrous boric oxide. This anhydrous boric oxide was prepared from the several times recrystallized hydrous boric acid by long-continued fusion over a blast lamp. A solution of approximately $\frac{n}{5}$ sodium hydroxide was prepared from the ordinary sodium hydroxide of the laboratory. The free alkali

* Jour. Am Chem. Soc., iv, 568.
† Zeitschr. f Anal. Chem., xxxvi (9), 568.
‡ Zeitschr. f. Anal. Chem, xxvi, 18.
§ Zeitschr. f. Anorg. Chem. (18). 549.
‖ J. S. C. I., xv, 432.
¶ Am. Chem. Jour., x, 154.
** J. Pharm. Chim. (6), viii, 109–111.
†† J. Prac. Chem., xxxviii, 118.
‡‡ Am. Chem. Jour, vi, 341.

in this solution was estimated by the process of Winkler recommended by Küsler. The acid used to make this estimation was hydrochloric, standardised by silver nitrate.

The full method for the estimation of boric acid as finally elaborated is as follows: The solution is made clearly acid to litmus by hydrochloric acid and 5^{cm^3} of a solution (10%) of barium chloride added. An amount of iodate and iodide of potassium sufficient to liberate an amount of iodine at least equivalent to the excess of hydrochloric acid in the acidified solution is mixed with starch in a separate beaker, and the iodine, which is usually thrown out by this mixture, is just bleached by a dilute solution of thiosulphate.

To the now neutral solution of iodide and iodate a single drop of the solution to be analyzed is transferred by a glass rod. If a blue coloration is developed, the solution is acidic with hydrochloric acid, and all the boric acid is in free condition. The amount of iodide and iodate used depends upon the acidity of the solution containing boric acid. Usually 10^{cm^3} of a 25 per cent solution of iodide and the same amount of a saturated solution of iodate is sufficient. Any larger excess of hydrochloric acid should be neutralized by sodium hydroxide before the iodide and iodate mixture is added. After the addition of the iodide and iodate solution, containing starch, to the boric acid solution, the liberated iodine should be carefully bleached by thiosulphate. Any excess of thiosulphate in reasonable amount does not seem to be detrimental, but in practice the starch iodide color is clearly bleached, and no more then added. Carbonates prevent a definite indication of the neutral point by thiosulphate and starch iodide, therefore the barium chloride (about 5^{cm^3}) should be added before this point in the process. The mixture of iodide and iodate is not added to the solution to be analyzed until after it is made acidic, for the reason that when the neutral point is approached by the addition of hydrochloric acid, the starch iodide is thrown out locally by the acid, and the small amount of sodium borate remaining undecomposed does not again bleach the coloration produced, thus obscuring the neutral point which must be obtained before titrating for boric acid.

The solution after the bleaching of the iodine by thiosulphate is colorless and contains only starch, neutral chloride, potassium tetrathionate, iodide and iodate, and all the boric acid present in uncombined condition. The carbonate lies out of the sphere of action in insoluble form as barium carbonate. A few drops of the indicator, phenolphthalein, are now added, and the alkaline solution run in until a strong red coloration is produced. A pinch of mannite is then added, which bleaches the phenolphthalein coloration, and the alkali solution again

run in to a faint indication, which if permanent on the addition of more mannite, may be taken as the reading point. About 1–2 grm of mannite are necessary for a determination. The boro-mannite compound is sufficiently acidic to liberate iodine abundantly, but it appears to be a time reaction, and at the end of six hours only about 95 per cent of the theoretical amount (considering B_2O_3 as a bivalent acid) has been thrown out. The combination of boric acid and mannite liberates in the presence of iodide and iodate immediately only about one-half the iodine required on the theory that B_2O_3 under these conditions acts as a bivalent acid, or with the neutralizing power of metaboric acid, HOBO. When no mannite is present phenolphthaline gives an alkaline indication when only about one-half the amount of alkali theoretically necessary to form the metaborate, NaOBO, has been added. Obviously, then, the starch iodide coloration will not appear at all on the addition of mannite, if about one-half the free boric acid is first neutralized by the solution of alkali, and the remainder of the alkali immediately added to complete neutralization. The point at which the danger of the appearance of the iodide coloration on the addition of mannite has been passed, is roughly indicated before the mannite has been added by the appearance of the strong alkaline indication of phenolphthalein. This indicator would not need to be added at all, if the boro-mannite compound quickly and regularly liberated iodine from the iodide and iodate. The fact, however, that this compound of boric acid and mannite—as has been ascertained by experiment—liberates, on standing twelve hours, about 99 per cent of the theoretical amount of iodine, places the strength of this acid above that of citric or tartaric acid as investigated by Furry.* With phenolphthalein, however, the end reaction is sharp and the small amount of carbonate present in the standard solution of alkali is precipitated by the barium chloride already in the solution. The calculation must therefore be based on the amount of free hydroxide in the standard solution of alkali used, according to the following representation:

$$B_2O_3 + 2NaOH = 2NaOBO + H_2O.$$

The best results and the most definite indications are obtained in cold solution of a volume not greater that 50^{cm^3}. This fact accords with the observations of Magnanini† that the relative electrical conductivity of the boro-mannite solution is decreased by dilution and elevation of the temperature. When silicates are present in solution, the

* Am. Chem. Jour., vi, 341.

† Gaz. Chim., xx, 428, and xxi, 134.

silicondioxide is liberated by the excess of hydrochloric acid, and this oxide, whether in hydrous or anhydrous condition, neither affects the indication with iodine nor phenolphthalein, nor does it form with mannite a compound of acidic properties. Ammonium salts interfere with the indication given by phenolphthalein and may be removed by boiling with potassium hydroxide in excess, or an indicator used not affected by them.

To test the action of fluorides in the process, several experiments were made in which hydrofluoric acid (10^{cm^3} of $\frac{n}{10}$ solution) was introduced into the solution containing salts of sodium, free hydrochloric and boric acids. Barium chloride was then added and the analysis for boric acid completed in the usual way without the accuracy of the results being in any way interfered with by the presence of hydrofluoric acid.

The following table contains the results of a series of analyses in which the boric acid was first drawn into an excess of sodium hydroxide, then estimated according to the method described.

The standard solutions of boric acid used contained I, 7·153 grm. and II, 7·706 grm. per liter. The solution of free sodium hydroxide was 0·21427 normal.

TABLE I.

		B_2O_3 Sol. taken. cm^3	NaOH Sol. required. cm^3	B_2O_3 taken. grm.	B_2O_3 found. grm.	Errors on B_2O_3. grm.
I.	(1)	21·95	21·02	0·1571	0·1577	+0·0006
	(2)	20·68	19·65	0·1479	0·1474	−0·0005
	(3)	20·73	19·63	0·1483	0·1473	−0·0010
II.	(4)	23·05	23·71	0·1776	0·1777	+0·0001
	(5)	23·10	23·80	0·1780	0·1783	+0·0003
	(6)	22·76	23·35	0·1754	0·1750	−0·0004
	(7)	24·08	24·78	0·1855	0·1857	+0·0002
	(8)	22·00	22·50	0·1695	0·1686	−0·0009
	(9)	20·78	21·28	0·1601	0·1595	−0·0006

Practical tests of the method were made upon specimens of crude calcium borate and colemanite.*

The finely-ground minerals were dissolved in hydrochloric acid and the analyses proceeded with as above described.

* These specimens were kindly furnished by Dr. C. A. Crampton, of Washington, whom I desire to thank for this courtesy.

Analysis of crude borate of lime.

TABLE II.

	Ca borate taken. grm.	B_2O_3 found. grm.	B_2O_3 in %.
(1)	0·4016	0·2289	56·99
(2)	0·4044	0·2302	56·92
(3)	0·4000	0·2285	57·11

Analysis of Colemanite.

TABLE III.

	Mineral taken. grm.	B_2O_3 found. grm.	% B_2O_3.	
(1)	0·4034	0·2064	51·15	
(2)	0·4070	0·2069	50·83	
(3)	0·6004	0·3054	50·86	Average. 50·99%
(4)	0·6006	0·3056	50·89	
(5)	0·5059	0·2592	51·24	
(6)	0·5092	0·2592	50·89	

An analysis for boric acid by this process can be completed in five minutes and the results are obviously accurate within the limits of ordinary analysis.

The usually interfering substances, fluorine, silica, and carbon dioxide, have no detrimental influence on the results of this process.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *On the Molecular Masses of Gases.*—It has been shown by D. Berthelot that in consequence of the difference between the coefficients of expansion and compressibility, the molecular masses of gases are proportional, not to the actual density, but to the product of this value into the molecular volume. The molecular volume of a gas is given by the formula $v_o = v\frac{p}{p_o}[1+a(p-p_o)] = v\frac{p}{p_o}(1+ap-ap_o)$; in which v is the actual volume under an infinitely small pressure p, p_o is the normal pressure, and a is a coefficient, constant, according to Regnault between 1 and 6 atmospheres and according to Amagat, below one atmosphere. When p_o is one atmosphere and p is indefinitely small, the ratio between the molecular volumes of two gases is $v_o/v'_o = (1-a)/(1-a')$. If their densities be d and d' their molecular masses are proportional to $(1-a)\,d$ and $(1-a')\,d'$. In the table below, the value of a at 0°, the molecular volume v_m at 0° and one atmosphere, the specific gravity d, oxygen being taken as a standard, the molecular mass M when O = 32 and the atomic mass μ when O = 16, are given as calculated:

	H	N	CO	O
a	−0·00046	+0·00038	+0·00046	+0·00076
v_m.....	1·00046	0·99962	0·99954	0·99924
d	0·062865	0·87508	0·87495	1·0
M	2·01472	28·0132	28·0068	32
μ	1·0074	14·007	12·007	16

The author compares the atomic masses of hydrogen, nitrogen, carbon and oxygen deduced as above from the molecular volumes and relative densities, with the best determinations of these values by chemical methods, and shows that they are almost identical.

	O	H	N	C
Physical method,	16	1·0074	14·007	12·007
Chemical method,	16	1·0023—1·0075	14·012	12·001—12·005

It would appear therefore that not only do the values of the atomic masses obtained from relative density and compressibility confirm the results obtained by chemical methods, but that in some cases they may be taken as the more reliable of the two.—*C. R.*, cxxvi, 954–956, 1030–1033, March, April, 1898. G. F. B.

2. *On the Preparation of Metals and Alloys by means of Aluminum.* — The commercial production of aluminum on a large scale has rendered it possible to make use of this metal for the reduction of the oxides and chlorides of other metals.

Experiments by GOLDSCHMIDT have greatly improved the earlier processes, by showing that it is not necessary to heat the crucible containing the mixture, from the outside, as in a furnace. It is quite sufficient to inflame this mixture at a single point, from which the action spreads more or less quickly throughout the mass. The ignition may be effected by means of a piece of magnesium wire inserted in the mass and lighted by a match. For mixtures of higher igniting points, a primer made by mixing aluminum powder with a substance easily giving up oxygen, such as lead or manganese peroxide, lead or copper oxide, may be placed on the mixture and this inflamed by the magnesium wire. Since the temperature of the reaction is intense, it is best to line the crucible with a refractory material such as magnesia or alumina, or in some cases the oxide of the metal that is to be reduced. The process may be modified by igniting first a small quantity of the mixture in the crucible, and then adding additional portions from time to time. The metals thus obtained are free from carbon and from carbide, and from aluminum also if the oxide is present in excess. In the case of chromium, the temperature reached was found approximately to be 3000°. The fused chromium thus prepared is permanent even in the air of the laboratory, behaving like a noble metal. Fused manganese resembles bismuth, showing surface colors. By this process, alloys of iron with 20 to 25 per cent of boron and with 40 per cent of titanium have been prepared; and also copper containing 10 per cent of chromium. An alloy of lead and barium decomposes water. Sulphides may be reduced in this way and at a lower temperature. The resulting slag when oxides are used is fused alumina, so hard as scarcely to be scratched by the diamond. In preparing chromium, minute transparent red crystals, resembling rubies, are found in it.—*Liebig's Annalen*, ccci, 19, June, 1898. G. F. B.

3. *On the Electrolytic Preparation of Beryllium.*—It has been shown by LEBEAU that beryllium fluoride, while a non-conductor of electricity when fused, becomes a conductor and an electrolyte when mixed with an alkali fluoride. Two beryllium-sodium fluorides, $BeF(NaF)_2$ and $BeF.NaF$, are available for this purpose. They are most easily prepared by dissolving beryllium hydrate and sodium carbonate, in the required proportions, in hydrogen fluoride and evaporating. The first of these double chlorides fuses at about 350° and the other at about redness. The salt to be reduced is melted in a nickel crucible, acting as the cathode, a rod of graphitic carbon serving as the anode. As soon as the current passes, the external source of heat is withdrawn, the temperature, which should not be allowed to rise above a low red heat, being thereafter maintained electrically. A current of 6 to 7 amperes is required, at an electromotive force of 30 to 40 volts; the metal separating in the crystalline form. If the electrolysis is conducted in a carbon crucible, which contains the other metal in the fused state, and which

serves as the anode, alloys of beryllium may be obtained.—*C. R.*, cxxvi, 744–746, March, 1898. G. F. B.

4. *On Colloidal Silver.*—Some experiments have been made by LOTTERMOSER and VON MEYER on the action of various reagents on colloidal silver. They find that acids precipitate it from solution in the "molecular" state, time and dilution being of great importance. To study the influence of time on the change from the colloidal to the molecular condition, a known amount of acid was added to the colloidal solution and the time was observed which was required for the complete change. By placing a drop of the solution on a glass plate resting on white paper, the end of the reaction is easily detected; the time being noted as soon as the separation of fine silver particles can be readily seen. The results of the experiments are given in a table. They show that the less the amount of acid used the longer the time required for the reaction. Moreover, the amount of acid required to produce the change in a given time appears to be inversely as the concentration of the solution. As to the precipitation of colloidal silver by salts of the heavy metals, experiment shows that where reducible metallic chlorides are used there is formed silver chloride and a lower chloride of the metal; a portion of the silver, however, being always precipitated in the insoluble form. If the solution of colloidal silver and of the metallic chloride are both very dilute, it frequently happens that neither silver chloride nor the lower metallic chloride is precipitated, both remaining in solution in the colloidal form. This behavior is particularly shown by mercuric chloride. Neither the chloride, bromide or iodide of colloidal silver appears to have any application in photography, though the iodide is of interest therapeutically.—*J. pr. Ch.*, II, lvi, 241, 1897; lvii, 540, July, 1898. G. F. B.

5. *On Silver peroxide and peroxynitrate.*—In continuing his researches on the higher oxide of silver and its compounds MULDER has observed that when the substance Ag_7NO_{11} is deprived of an atom of oxygen and the residue is extracted with water, silver nitrate goes into solution and silver peroxide Ag_2O_2 remains. Since the silver nitrate can be extracted in a short time, the nitrate Ag_7NO_{11} may be regarded as having the composition $(Ag_2O_2)_3 . AgNO_5$. When boiled with water the peroxynitrate is decomposed, oxygen is set free and silver nitrate goes into solution, leaving a residue of silver peroxide. This suggests a convenient method for preparing the peroxide. This higher oxide dissolves in concentrated sulphuric and in concentrated nitric acid, giving brown solutions. The presence of water accelerates the decomposition of these solutions. The peroxide is not soluble in acetic acid though when diluted silver acetate and oxygen are formed. A method for determining the excess of oxygen in the peroxynitrate is described, based on the decomposition of this salt by water. When kept for some time the peroxynitrate undergoes slow spontaneous decomposition even over sulphuric acid. So slow is this change, however, that the author estimates that it

would require about 13 years to eliminate the two atoms of oxygen in excess.—*Rev. Trav. Chim.*, xvii, 129–176, 1898; *J. Chem. Soc.*, lxxiv, ii, 516, Nov. 1898. G. F. B.

6. *On Neodymium.*—According to BOUDOUARD, neodymium can be isolated by allowing a solution of the pure sulphates of the yttrium metals to remain in contact with potassium sulphate in excess for at least 24 hours, then decomposing the insoluble double sulphate thus produced, with sodium hydrate, dissolving the oxide in nitric acid and precipitating with oxalic acid. The substance thus prepared afforded the atomic mass 143, agreeing well with 142·7 ordinarily assigned to this metal. The oxide is greenish, while the oxalate and anhydrous sulphate are slightly rose-colored. The crystallized sulphate, also rose-colored, while less soluble than the anhydrous sulphate, is more soluble in cold water than in hot. A solution of the sulphate gives an absorption spectrum having a shadow from 591·5 to 584, an intense band from 584 to 572, another from 523 to 519, a feeble band from 512 to 508, and faint bands at 480 and 470, due probably to traces of praseodymium. The double sulphate of potassium and neodymium is more soluble than the corresponding compound of praseodymium.—*C. R.*, cxxvi, 900–901, March, 1898. G. F. B.

7. *Leçons de Chimie Physique professées à l'Université de Berlin;* par J. H. VAN'T HOFF, Professeur ordinaire à l'Université, etc. Ouvrage traduit de l'allemande par M. Corvisy. Première Partie, La Dynamique Chimique. 8vo, pp. 263. Paris, 1898 (A. Hermann).—The lectures delivered by Professor Van't Hoff during 1897 were upon "Selected subjects in Physical Chemistry" and were divided into three parts, the first comprising Chemical Dynamics, the second Chemical Statics, and the third Relations between the Properties of Substances and their Composition. The present volume contains the first part only; and like all the productions of this eminent authority, is full of the most valuable material admirably classified and clearly treated. The subject is divided into two principal sections, the first on Chemical Equilibrium and the second on Speed of Reaction; each of these being subdivided into two parts, the former section into Chemical Equilibrium in its Physical and especially its Thermodynamic relations and Chemical Equilibrium in its Mechanical and Molecular relations; and the latter section into Theoretical laws of reaction speeds and Experimental results of Reaction speeds. The translator seems to have done his work with care and thus to have made available this excellent presentation of the subject to a much larger class of students. G. F. B.

8. *Outlines of Industrial Chemistry;* a Text-book for Students. By FRANK HALL THORP, Ph.D. 8vo, pp. xx, 541. New York, 1898 (The Macmillan Company).—Dr. Thorp has given us in this book a compendium of commercial chemical processes which cannot fail to be of use to the technical student. The first part is devoted to Inorganic industries such as relate to fuels, waters, the soda industry, the chlorine industry, fertilizers, cements, glass

and ceramics, pigments, etc. The second part treats of Organic industries, connected with the destructive distillation of wood, bones and coal, with mineral oils, with vegetable and animal oils and soaps, with the sugars and fermentation, with explosives, textiles, etc. The volume is well printed and illustrated. G. F. B.

9. *Charge of Electricity carried by the ions produced by Röntgen Rays.*—Mr. C. T. R. Wilson (Phil. Trans. A., 1897, p. 265) has discovered that Röntgen rays can produce a cloudy condensation in dust-free air when the latter is subjected to a sudden expansion. This condensation cannot be produced by expansion without the aid of the rays. Prof. J. J. THOMSON has made use of this phenomenon to determine the value of the product $n\,e\,v$ where n is the number of ions in unit volume of the gas, e the charge in an ion, v the mean velocity of the positive and negative ions under a definite electromotive force. The size of the drops was determined from the expression $v = \frac{2\,g a^2}{9\,\mu}$ in which g is the acceleration of gravitation; a, the radius of the drop around the ions as nuclei, μ the coefficient of viscosity of the gas through which the drops fell. The velocity was determined by observing the time the top layer of the cloud took to fall a given distance.

The mean value of the charge on the ion was found to be $6{\cdot}5 \times 10^{-10}$. The experiments seemed to show that the charge on the ions in hydrogen was the same as in air. From the laws of electrolysis, if e is the charge on the hydrogen ion in electrostatic units, N the number of molecules in 1 cub. centim. at standard temperature and pressure,

$$Ne = 129 \times 10^{8}.$$

If e is taken as $6{\cdot}5 \times 10^{-10}$

$$N = 20 \times 10^{18}$$

When N deduced from experiments on viscosity of air is 21×10^{18}. The agreement between the value of N got by the kinetic theory of gases by viscosity experiments and the value obtained by Professor Thomson's experiments, leads him to believe that the theory is consistent with the value he has obtained for e, being equal to or of the same order, as the charge carried by the hydrogen ion in electrolysis.—*Phil. Mag.*, Dec. 1898, pp. 528–545. J. T.

10. *Use of the Coherer in Measuring Electric Waves.*—It is still a disputed question whether the coherer can be used in the investigation of stationary electric waves. Professor Murani, of Milan, has published an investigation which seems to show that the coherer is too sensitive to such waves, and that having responded to the first electric impulse it is no longer sensitive to succeeding ones. One thus obtains a more or less constant deflection through a galvanometer in the coherer circuit without any evidence of nodes or ventral segments. O. BEHRENDSEN believes that better results can be obtained by using a comparatively insensitive coherer, which will only respond to the integrated im-

pulses. He makes such a coherer out of comparatively fine carbon powder. By means of such a coherer he obtained evidences of interference phenomena. With a sensitive coherer filled with nickel filings he measured the dimension of electric waves produced by interference in passing through a metallic grating. — *Wied. Ann.*, No. 13, 1898, pp. 1024–1029. J. T.

11. *Color Blindness and the Röntgen Rays.*—E. DORN has investigated the sensitiveness of the eyes of a totally color-blind person to the Röntgen rays. He believes that the light seen by the color-blind person when the eye is exposed to the rays is not due to a fluorescence excited in the retina by these rays, but is due to a peculiar aptitude of the eyes to perceive these rays. The light excited by the rays is greatest at the periphery of the eye; this indicates that the rods of the eye are sensitive to the Röntgen rays. The author then sought to answer the question whether the cones are also sensitive. He discovered that these are also sensitive and no central blind spot insensitive to these rays could be found in the totally color-blind eye. His experiments he believes can be used to disprove the hypothesis that total color-blindness can be ascribed either to failure or the aptitude of the cones of the eye.— *Wied. Ann.*, No. 13, 1898, pp. 1170–1176. J. T.

12. *Regenerating Vacuum Tubes;* by W. ROLLINS. (Communicated.)—In an interesting article in the January number of this Journal on absorption of gases in a high vacuum, Prof. C. C. Hutchins states that after a short period of work the vacuum in a Röntgen tube becomes too high. He then considers the causes of the rise and discusses the various methods for increasing the pressure, recommending oxygen as the most suitable gas because its absorption is slow. The use of oxygen is not new; tubes with adjustable oxygen vacuums were made soon after Röntgen's discovery was announced and were described in a series of notes on Röntgen light in the Electrical Review in 1897–8, and are illustrated in Kirmayer and Oelling's catalogue. In this connection it may be well to state that regenerative tubes with hydrogen vacuums have been recently recommended by Villard, who attaches a closed platinum tube which is heated in a Bunsen flame when it is desired to increase the pressure in the Röntgen tube. A regenerating tube of this kind was described in 1897 in the above-mentioned notes, which was superior to the more recent form, because the hollow platinum tube was used as a target for the impact of the cathode discharge. As this hollow target could be cooled, a large amperage could be used. To increase the pressure it is only necessary to put a drop of liquid hydrocarbon into the hollow target and heat it with the cathode discharge, or illuminating gas can be used, retaining it temporarily in place with a bit of cork.

In some of my experiments I tried a plan used by Professor Trowbridge soon after Röntgen's discovery was announced, but now lost sight of, which consisted in cooling the discharge tube

in oil. When this method is applied to a hollow target tube the fresh, cool oil must be made to constantly strike against the back of the target, otherwise this will get red hot and drive back the oil, the hydrogen passing through the platinum. In this way I have had the vacuum change from fifteen inches to one-sixteenth of an inch equivalent air-spark in a short time.

What those of us who are trying to use Röntgen's discovery in medical diagnosis want, is not rediscoveries, but to have placed within our reach apparatus which will convert into Röntgen light an appreciable amount of the energy put into it. At present we may pour in at one end energy at the rate of ten amperes at one hundred volts, and when we come to take it out at the other end as Röntgen radiation there will not be enough with good definition to clearly see through the abdomen. If some broad commercial use could be found for Röntgen's discovery, then the great inventors would attack the problem. At present a tallow candle, notwithstanding its thermic waste, is as a converter of energy into light a shining success compared with the best available Röntgen apparatus. The only notable advance which has been made in practice is due to M. Tesla, but even he seems unable to give much time to this matter; as a result, neither he nor anyone knows when his apparatus will be commercially available. Even when we get it the results will probably be far below the possibilities of the method as shown by the hints dropped from time to time by prominent physicists. Take, for example, Professor Trowbridge's statement that he had made a photograph of the bones of a hand in one-millionth of a second. With the best available apparatus the exposure must be from sixty million to three hundred million times as long. Part of the advance which will be made must consist in devising simple means of making the exciting surges harmonics of the rate of vibration we wish to produce in the radiant energy. All my experiments point in this direction, and I find it practical to get a better result with a small properly-tuned generator than with the largest size improperly adjusted, but I know too little of physics to make any important advance in this matter.

II. Geology and Natural History.

1. *The Age of the Earth.*—The January number of the Philosophical Magazine contains a notable article by Lord Kelvin, on the age of the earth as an abode fitted for life. This is an extension of the Victoria Institute Annual Address for 1897. The opening pages give an interesting account of the early attitude of the geologist to the subject in demanding almost unlimited time for the geological changes the earth has gone through and for the development of life. Then follows a summary of the arguments by which the author showed (1862 to 1869) the strict limitations of the possible age of earth, viewed as an abode for life, and arrived at the conclusion that the earth's consolidation

could not have taken place less than 20 million, nor more than 400 million years ago. With respect to this he adds:

"During the 35 years which have passed since I gave this wide-ranged estimate, experimental investigation has supplied much of the knowledge then wanting regarding the thermal properties of rocks to form a closer estimate of the time which has passed since the consolidation of the earth, and we have now good reason for judging that it was more than 20 and less than 40 million years ago; and probably much nearer 20 than 40."

Remarking upon the conclusion reached by Mr. Clarence King (this Journal, Jan., 1893), based largely upon the experimental data supplied by Dr. Carl Barus, in the laboratory of the U. S. Geological Survey, that "we have no warrant for extending the earth's age beyond 24 million of years," he adds that the results of his own recent calculations lead to an estimate not differing much from this.

Going on to discuss the course of events following the first solidification of the earth's surface, the author says:

"§ 21. I have given strong reasons* for believing that *immediately* before solidification at the surface, the interior was solid close up to the surface: except comparatively small portions of lava or melted rock among the solid masses of denser solid rock which had sunk through the liquid, and possibly a somewhat large space around the center occupied by platinum, gold, silver, lead, copper, iron, and other dense metals, still remaining liquid under very high pressure."

"§ 22. I wish now to speak to you of depths below the great surface of liquid lava bounding the earth before consolidation; and of mountain heights and ocean depths formed probably a few years after a first emergence of solid rock from the liquid surface (see § 24, below), which must have been quickly followed by complete consolidation all round the globe." . . .

"§ 23. To prepare for considering consolidation at the surface let us go back to a time (probably not more than twenty years earlier as we shall presently see—§ 24) when the solid nucleus was covered with liquid lava to a depth of several kilometers; to fix our ideas let us say 40 kilometers (or 4 million centimeters). At this depth in lava, if of specific gravity 2·5, the hydrostatic pressure is 10 tons weight (10 million grammes) per square centimeter, or ten thousand atmospheres approximately. According to the laboratory experiments of Clarence King and Carl Barus† on diabase, and the thermodynamic theory‡ of my brother, the late

* "On the Secular Cooling of the Earth," vol. iii, Math. and Phys. Papers, §§ 19–33.

† Phil. Mag., 1893, first half-year, p. 306.

‡ Trans. Roy. Soc. Edinburgh, Jan. 2, 1849; Cambridge and Dublin Mathematical Journal, Nov., 1850. Reprinted in Math. and Phys. Papers (Kelvin), vol. i, p. 156.

Professor James Thomson, the melting temperature of diabase is 1170° C. at ordinary atmospheric pressure, and would be 1420° under the pressure of ten thousand atmospheres, if the rise of temperature with pressure followed the law of simple proportion up to so high a pressure."

"§ 24. The temperature of our 40 kilometers deep lava ocean of melted diabase may therefore be taken as but little less than 1420° from surface to bottom. Its surface would radiate heat out into space at some such rate as two (gramme-water) thermal units Centigrade per square centimeter per second.* Thus, in a year (31½ million seconds) 63 million thermal units would be lost per square centimeter from the surface. This is, according to Carl Barus, very nearly equal to the latent heat of fusion abandoned by a million cubic centimeters of melted diabase in solidifying into the glassy condition (pitch-stone) which is assumed when the freezing takes place in the course of a few minutes. But, as found by Sir James Hall in his Edinburgh experiments† of 100 years ago, when more than a few minutes is taken for the freezing, the solid formed is not a glass but a heterogeneous crystalline solid of rough fracture; and if a few hours or days, or any longer time, is taken, the solid formed has the well known rough crystalline structure of basaltic rocks found in all parts of the world. Now Carl Barus finds that basaltic diabase is 14 per cent denser than melted diabase, and 10 per cent denser than the glass produced by quick freezing of the liquid. He gives no data, nor do Rücker and Roberts-Austen, who have also experimented on the thermodynamic properties of melted basalt, give any data, as to the latent heat evolved in the consolidation of liquid lava into rock of basaltic quality. Guessing it as three times the latent heat of fusion of the diabase pitch-stone, I estimate a million cubic centimeters of liquid frozen per square centimeter per centimeter per three years. This would diminish the depth of the liquid at the rate of a million centimeters per three years, or 40 kilometers in twelve years."

"§ 25. Let us now consider in what manner this diminution of depth of the lava ocean must have proceeded, by the freezing of portions of it; all having been at temperatures very little below the assumed 1420° melting temperature of the bottom, when the depth was 40 kilometers. The loss of heat from the white-hot surface (temperatures from 1420° to perhaps 1380° in different parts) at our assumed rate of two (gramme-water Centigrade) thermal units per sq. cm. per sec. produces very rapid cooling of the liquid within a few centimeters of the surface

* This is a very rough estimate which I have formed from a consideration of J. T. Bottomley's accurate determinations in absolute measure of thermal radiation at temperatures up to 920° C. from platinum wire and from polished and blackened surfaces of various kinds in receivers of air-pumps exhausted down to one tenth-millionth of the atmospheric pressure. Phil. Trans. Roy. Soc., 1887 and 1893.

† Trans. Roy. Soc. Edinburgh.

(thermal capacity ·36 per gramme, according to Barus) and in consequence great downward rushes of this cooled liquid, and upwards of hot liquid, spreading out horizontally in all directions when it reaches the surface. When the sinking liquid gets within perhaps 20 or 10 or 5 kilometers of the bottom, its temperature* becomes the freezing-point as raised by the increased pressure; or, perhaps more correctly stated, a temperature at which some of its ingredients crystallize out of it. Hence, beginning a few kilometers above the bottom, we have a snow shower of solidified lava or of crystalline flakes, or prisms, or granules of feldspar, mica, hornblende, quartz, and other ingredients: each little crystal gaining mass and falling somewhat faster than the descending liquid around it, till it reaches the bottom. This process goes on until, by the heaping of the granules and crystals on the bottom, our lava ocean becomes silted up to the surface."

"*Probable Origin of Granite.*—§ 26. Upon the suppositions we have hitherto made, we have, at the stage now reached, all round the earth at the same time a red hot or white hot surface of solid granules or crystals with interstices filled by the mother liquor still liquid, but ready to freeze with the slightest cooling. The thermal conductivity of this heterogeneous mass, even before the freezing of the liquid part, is probably nearly the same as that of ordinary solid granite or basalt at a red heat, which is almost certainly† somewhat less than the thermal conductivity of igneous rocks at ordinary temperatures. If you wish to see for yourselves how quickly it would cool when wholly solidified, take a large macadamizing stone, and heat it red hot in an ordinary coal fire. Take it out with a pair of tongs and leave it on the hearth, or on a stone slab at a distance from the fire, and you will see that in a minute or two, or perhaps in less than a minute, it cools to below red heat."

"§ 27. Half an hour‡ after solidification reached up to the surface in any part of the earth, the mother liquor among the granules must have frozen to a depth of several centimeters below the surface and must have cemented together the granules and crystals, and so formed a crust of primeval granite, comparatively cool at its upper surface, and red hot to white hot, but still all solid, a little distance down; becoming thicker and thicker very rapidly at first; and after a few weeks certainly cold enough at its outer surface to be touched by the hand."

* The temperature of the sinking liquid rock rises in virtue of the increasing pressure: but much less than does the freezing point of the liquid or of some of its ingredients. (See Kelvin, Math. and Phys. Papers, vol. iii, pp. 69, 70.)

† Proc. Roy. Soc., May 30, 1895.

‡ Witness the rapid cooling of lava running red hot or white hot from a volcano, and after a few days or weeks presenting a black hard crust strong enough and cool enough to be walked over with impunity.

"*Probable Origin of Basaltic Rock.**—§ 28. We have hitherto left, without much consideration, the mother liquor among the crystalline granules at all depths below the bottom of our shoaling lava ocean. It was probably this interstitial mother liquor that was destined to form the basaltic rock of future geological time. Whatever be the shapes and sizes of the solid grauules when first falling to the bottom, they must have lain in loose heaps with a somewhat large proportion of space occupied by liquid among them. But, at considerable distances down in the heap, the weight of the superincumbent granules must tend to crush corners and edges into fine powder. If the snow shower had taken place in air we may feel pretty sure (even with the slight knowledge which we have of the hardness of the crystals of feldspar, mica and hornblende, and of the solid granules of quartz) that, at a depth of 10 kilometers, enough of matter from the corners and edges of the granules of different kinds, would have been crushed into powder of various degrees of fineness, to leave an exceedingly small proportionate volume of air in the interstices between the solid fragments. But in reality the effective weight of each solid particle, buoyed as it was by hydrostatic pressure of a liquid less dense than itself by not more than 20 or 15 or 10 per cent, cannot have been more than from about one-fifth to one-tenth of its weight in air, and therefore the same degree of crushing effect as would have been experienced at 10 kilometers with air in the interstices, must have been experienced only at depths of from 50 to 100 kilometers below the level of the lava ocean."

"§ 29. A result of this tremendous crushing together of the solid granules must have been to press out the liquid from among them, as water from a sponge, and cause it to pass upwards through the less and less closely packed heaps of solid particles, and out into the lava ocean above the heap. But, on account of

* Note by the Editor: An Addendum at the close of the paper quotes the following determination of melting points by Prof. Roberts-Austen:

	Melting-point.	Error.
Feldspar	1520° C.	±30°
Hornblende	about 1400°	
Mica	1440°	±30°
Quartz	1775°	±15°
Basalt	about 880°	

The author adds:

"These results are in conformity with what I have said in §§ 26–28 on the probable origin of granite and basalt, as they show that basalt melts at a much lower temperature than feldspar, hornblende, mica, or quartz, the crystalline ingredients of granite. In the electrolytic process for producing aluminium, now practised by the British Aluminium Company at their Foyers works, alumina, of which the melting-point is certainly above 1700° C. or 1800° C., is dissolved in a bath of melted cryolite at a temperature of about 800° C. So we may imagine melted basalt to be a solvent for feldspar, hornblende, mica, and quartz at temperatures much below their own separate melting-points; and we can understand how the basaltic rocks of the earth may have resulted from the solidification of the mother liquor from which the crystalline ingredients of granite have been deposited."

the great resistance against the liquid permeating upwards 30 or 40 kilometers through interstices among the solid granules, this process must have gone on somewhat slowly; and, during all the time of the shoaling of the larva ocean, there may have been a considerable proportion of the whole volume occupied by the mother liquor among the solid granules, down to even as low as 50 or 100 kilometers below the top of the heap, or bottom of the ocean, at each instant. When consolidation reached the surface, the oozing upwards of the mother liquor must have been still going on to some degree. Thus, probably for a few years after the first consolidation at the surface not probably for as long as one hundred years, the settlement of the solid structure by mere mechanical crushing of the corners and edges of solid granules, may have continued to cause the oozing upwards of mother liquor to the surface through cracks in the first formed granite crust and through fresh cracks in basaltic crust subsequently formed above it."

After a further discussion of the probable origin of continents and ocean depths, and also of the earth's atmosphere, the author concludes as follows:

"43. Whatever may have been the true history of our atmosphere it seems certain that if sunlight was ready, the earth was ready, both for vegetable and animal life, if not within a century, at all events within a few hundred centuries after the rocky consolidation of its surface. But was the sun ready? The well founded dynamical theory of the sun's heat carefully worked out and discussed by Helmholtz, Newcomb, and myself,* says NO if the consolidation of the earth took place as long ago as 50 million years; the solid earth must in that case have waited 20 or 50 million years for the sun to be anything nearly as warm as he is at present. If the consolidation of the earth was finished 20 or 25 million years ago, the sun was probably ready,—though probably not then quite so warm as at present, yet warm enough to support some kind of vegetable and animal life on the earth."

"§ 44. My task has been rigorously confined to what, humanly speaking, we may call the fortuitous concourse of atoms, in the preparation of the earth as an abode fitted for life, except in so far as I have referred to vegetation, as possibly having been concerned in the preparation of an atmosphere suitable for animal life as we now have it. Mathematics and dynamics fail us when we contemplate the earth, fitted for life but lifeless, and try to imagine the commencement of life upon it. This certainly did not take place by any action of chemistry, or electricity, or crystalline grouping of molecules under the influence of force, or by any possible kind of fortuitous concourse of atoms. We must pause, face to face with the mystery and miracle of the creation of living creatures."

* See "Popular Lectures and Addresses," vol. i, pp. 376–429, particularly page 397.

2. *Recent Publications of the U. S. Geological Survey:** ANNUAL REPORTS.—The five parts (making 6 volumes) of the *18th Annual Report* are now complete. All have been noticed excepting the following papers included in parts II and III:

The Triassic Formations of Connecticut, by W. M. Davis. Pt. II, pp. 1 to 192, 20 pls. including folded map and sections.

Geology of the Edwards Plateau and Rio Grande Plain adjacent to Austin and San Antonio, Texas, with reference to the occurrence of underground waters, by R. T. Hill and T. W. Vaughan. Pt. II, pp. 193–321, pls. 31.

A Table of the North American Tertiary Horizons, correlated with one another and with those of Western Europe, with annotations, by W. H. Dall. Pt. II, pp. 323 to 348.

Glaciers of Mount Rainier, by I. C. Russell, with a paper on *The Rocks of Mount Rainier*, by G. O. Smith. Pt. II, pp. 349 to 423, pls. 18.

The Age of the Franklin White Limestone of Sussex County, New Jersey, by J. E. Wolff and A. H. Brooks. Pt. II, pp. 425 to 457, with geological map.

A Geological Sketch of San Clemente Island, by W. S. T. Smith. Pt. II, pp. 459 to 496, pls. 13.

Geology of the Cape Cod District, by N. S. Shaler. Pt. II, pp. 497 to 593, pls. 8.

Recent Earth Movement in the Great Lakes Region, by G. K. Gilbert. Pt. II, pp. 595 to 647, pl. 1.

Some Coal Fields of Puget Sound, by Bailey Willis. Pt. III, pp. 393 to 436, 17 pls.

Geology and Mineral Resources of the Judith Mountains of Montana, by W. H. Weed and L. V. Pirsson. Pt. III, pp. 439 to 616, 18 pls. including maps. See this Journal, vol. vi, p. 508, December, 1898.

The Mining Districts of the Idaho Basin and the Boise Ridge, Idaho, by Waldemar Lindgren, with a report on fossil plants by F. H. Knowlton. Pt. III, pp. 619 to 794, pls. 16.

Preliminary Report on the Mining Industries of the Telluride Quadrangle, Colorado, by C. W. Purington. Pt. III, pp. 745 to 850. The areal geology of this quadrangle is given by Mr. Cross in plate ciii.

The Nineteenth Annual Report (1897–98) will appear in six parts (seven volumes). The report of the Director C. D. Walcott of Part I, pp. 143 with two folded maps, giving an account of the operations of the Survey to June 30, 1898, is already issued. The total appropriation for the work of the Survey was $1,033,963.60. Besides continuing the work already begun along essentially the same lines, this increased appropriation provided for the Survey of Forest Reserves, the boundary line between Idaho and Montana and the extension of work in Alaska. Mineral Resources for

* Issued since March, 1898. For last complete list and references to earlier ones see this Journal for April, 1898, p. 303; notices published since this date are referred to under the respective titles.

1897, forming Part VI of the Nineteenth Annual Report, will appear in two volumes; the first including Metallic Products, Coal and Coke, the second, Non-Metallic Products excepting Coal and Coke. Separates are nearly all issued and volumes will soon appear.

MONOGRAPHS: Fossil Medusæ Mon. xxx, by C. D. Walcott, pp. 201, pls. 47. See this Journal, December, 1898, p. 508.

BULLETINS: *The Cretaceous Foraminifera of New Jersey*, by R. M. Bagg, Jr. Bull. No. 88, pp. 89, pls. 6.

Some Lava Flows of the Western Slope of the Sierra Nevada, California, by F. L. Ransome, Bull. 89, pp. 73. See this Journal for December, 1898, p. 509.

Bibliography and Index of North American Geology, Paleontology, Petrology and Mineralogy, by F. B. Weeks, Bull. No. 149, pp. 152, for 1896; Bull. 156, pp. 130, for 1897.

The Educational Series of Rock Specimens collected and distributed by the U. S. Geological Survey, by J. S. Diller, Bull. 150, pp. 400, pls. 47. See this Journal, January, 1899, p. 74.

The Lower Cretaceous Gryphæas of the Texas Region, by R. T. Hill and T. W. Vaughan, Bull. No. 151, pp. 138, pls. 35. See this Journal, January, 1899, p. 70.

A Catalogue of Cretaceous and Tertiary Plants of North America, by F. H. Knowlton, Bull. 152, pp. 247.

A Bibliographic Index of North American Carboniferous Invertebrates, by Stuart Wheeler, Bull. No. 153, pp. 653.

A Gazetteer of Kansas, by Henry Gannett, Bull. No. 154, pp. 246, with map of the State.

Earthquakes in California in 1896 and 1897, by C. D. Perrine, Bull. 155, pp. 45.

WATER SUPPLY AND IRRIGATION PAPERS: No. 12, *Underground Waters of a portion of Southeastern Nebraska*, by N. H. Darton, pp. 56, pls. 21.

No. 13, *Irrigation Systems in Texas*, by W. F. Hutson, pp. 68, pls. 10.

No. 14, *Tests of Pumps and Water Lifts*, by O. P. Hood, pp. 91, pl. 1.

Nos. 15 and 16, *Operations at River Stations in 1897*, Parts I and II, by F. H. Newell, pp. 200.

No. 17, *Irrigation near Bakerfield, California*, by C. E. Grunsky, pp. 96, pls. 16.

No. 18, *Irrigation near Fresno, California*, by C. E. Grunsky, pp. 94, pls. 14.

Geologic Folios: No. 38, Butte Special, Montana, Long. 112° 29′ 30″ to 112° 36′ 42″, Lat. 45° 39′ 28″ to 46° 02′ 54″, by S. F. Emmons and G. W. Tower, Jr.

No. 39, Truckee, California, Long. 120° to 120° 30′, Lat. 39° to 39° 30′, by Waldemar Lindgren.

No. 40, Wartburg, Tennessee, Long. 84° 30′ to 85°, Lat. 36° to 36° 30′, by Arthur Keith.

No. 41, Sonora, California, Long. 120° to 120° 30′, Lat. 37° 30′ to 38°, by H. W. Turner and F. L. Ransome.

No. 42, Neuces, Texas, Long. 100° to 100° 30′, Lat. 29° 30′ to 30°, by R. T. Hill and T. W. Vaughan.

No. 43, Bidwell Bar, California, Long. 121° to 121° 30′, Lat. 39° 30′ to 40°, by H. W. Turner.

No. 44, Tazwell, West Virginia, Long. 81° 30′ to 82°, Lat. 37° to 37° 30′, by M. R. Campbell.

No. 45, Boise, Idaho, Long. 116° to 116° 30′, Lat. 43° 30′ to 44°, by Waldemar Lindgren.

No. 46, Richmond, Kentucky, Long. 84° to 84° 30′, Lat. 37° 30′ to 38°, by M. R. Campbell.

Topographic Folios: Physiographic Types by Henry Gannett. See this Journal for July, 1898, p. 102. J. S. D.

3. *A Catalogue of the Cretaceous and Tertiary plants of North America;* by F. H. Knowlton, pp. 1–247, 1898, U. S. Geological Survey, Bulletin 152.—Mr. Knowlton has furnished paleobotanists a valuable aid to study by publishing this working catalogue of the known American species of Cretaceous and Tertiary plants, without waiting to make it absolutely perfect. Systematic names are checked back as far as the Kew Index for genera found also living, and to original source of description for species and the more important references to later descriptions or illustrations. Also the matters of geographical distribution and geological range are given so far as commonly reported in the literature, while the full knowledge regarding these points is left for future investigation. The Bibliography is a list of the papers consulted without assuming that it is a complete list.

4. *Iowa Geological Survey. Annual Report, 1897, with accompanying papers.* Samuel Calvin, State Geologist, vol. viii, pp. 1–427, plates 1–xxxii, figures 1–13, and six maps, 1898.—This eighth volume contains detailed reports of the areal geology and, where ascertained, the faunal lists of fossil species for the counties of Dallas, Delaware, Buchanan, Decatur and Plymouth, with excellent colored maps and frequent half-tone views of important rock sections and landscapes. H. F. Bain contributes a chapter on Properties and Tests of Iowa Building stones. H. S. W.

5. *A Preliminary Report on a Part of the Gold Deposits of Georgia;* by W. S. Yeates, State Geologist, and S. W. McCallie and Francis P. King, Assistant Geologists. 1896. Geological Survey of Georgia, W. S. Yeates, State Geologist. Bulletin No. 4-A.—This handsome and well illustrated volume of 542 pages gives an account of the various gold deposits of Georgia, especially with reference to their present development. As is well known, these lie chiefly on lines running northeast and southwest, in the northern part of the State: Some fifty years since, the amount of gold annually coined at the State mint amounted to nearly or quite $500,000; but since the exhaustion of the placer mines, from which most of the gold had been derived, the output has fallen off very largely, and in 1895 the total production of

gold (and silver) is estimated as but $128,000. The geologist, however, expresses the opinion that with the deep-mining and economic working of refractory ores now being introduced, the future outlook is promising, and the production may be expected to reach what it was in former years.

6. *The Report of the Governor of Arizona to the Secretary of the Interior*, for the fiscal year ending June 30th, 1898.—This report, in addition to the discussion of various economic and agricultural subjects of importance especially to the community involved, contains also a detailed account of the distribution of the metallic wealth of the Territory, by W. P. Blake, Territorial Geologist. How varied and extensive the metallic products of Arizona are, is well understood, and this fact gives much interest to this account of the various gold fields, the mines of silver and argentiferous lead, of copper not the least important of the metals, also coal, marble and other mineral products. It is interesting to note that the production of copper in Arizona has been increased fourfold since 1883, and for the first six months of 1898, amounted to nearly 20 per cent of the entire production of the United States.

7. *Die natürlichen Pflanzenfamilien, Lieferung* 182, 183, *Leipzig*, 1898.—Professor ENGLER has carried this important work nearly to completion. The present installments comprise a portion of one of the indexes; a general index is to follow at the close. Certain of the groups of Cryptogams are still in arrears, but they cannot be much longer delayed. The wealth of illustrations, the general treatment of orders, and the skill with which minor references to distribution and use have been employed, make the whole work a treasury for general and special botanists. Under the conditions of publication, it was impossible to avoid the unfortunate separation of subjects which should have been united, but these annoyances are now likely to be forgotten by all the patient subscribers. There cannot be one of these subscribers who does not feel that he has obtained far more than the worth of his money in these clearly printed and attractive volumes.

G. L. G.

8. *The Fishes of North and Middle America.* A descriptive catalogue of the species of fish-like vetebrates found in the waters of North America, north of the Isthmus of Panama; by DAVID STARR JORDAN and BARTON WARREN EVERMANN. Part III, pp. i–xxiv, 2183–3136. Washington, 1898 (Smithsonian Institution: Bulletin of the U. S. National Museum, No. 47).—The third part of this exhaustive Memoir on the Fishes of North America, mentioned on page 79 of the last number, has now appeared. Pages 2183 to 2873 are devoted to the description of species, and the remainder of the volume is given to a key to the families of the true fishes or Teleostei, the glossary of technical terms and the index.

III. Miscellaneous Scientific Intelligence.

1. *Ostwald's Klassiker der Exakten Wissenschaften.*—The latest additions to this valuable series of scientific classics are Nos. 97 to 103, whose titles are given below. We have often had occasion to call attention to this series before, and its value must now be well appreciated by all of those interested in physics and physical work. It would be difficult to overestimate the importance to the physical student of having before him such papers as are here brought together. They are all of the highest character, and a large part of them, as originally published, are comparatively inaccessible; but they are here republished in convenient form, ready for the student in his study, or the worker in the laboratory. Space forbids any separate notice of the individual memoirs here mentioned, and indeed this is unnecessary, since they are too well known to require it. Ostwald's Series gains additional interest from the fact that an undertaking on somewhat similar lines is being carried forward in this country (already noticed in this Journal), as Harper's Scientific Memoirs, edited by Professor Ames of Baltimore.

Nr. 97. Sir Isaac Newton's Optik oder Abhandlung über Spiegelungen, Brechungen, Beugungen und Farben des Lichts. (1704) II und III Buch.

Nr. 98. Ueber das Benzin und die Verbindungen desselben. Von Eilhard Mitscherlich. (1834.)

Nr. 99. Ueber die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen. Von R. Clausius. (1850.)

Nr. 100. Abhandlungen über Emission und Absorption von G. Kirchhoff.

I. Ueber die Fraunhofer'schen Linien. (1859.)

II. Ueber den Zusammenhang zwischen Emission und Absorption von Licht und Wärme (1859.)

III. Ueber das Verhältniss zwischen dem Emissionsvermögen und dem Absorptionsvermögen der Körper für Wärme und Licht (1860–1862.)

Nr. 101. Abhandlungen über Mechanische Wärmetheorie von G. Kirchhoff.

I. Ueber einen Satz der mechanischen Wärmetheorie und einige Anwendungen desselben. (1858.)

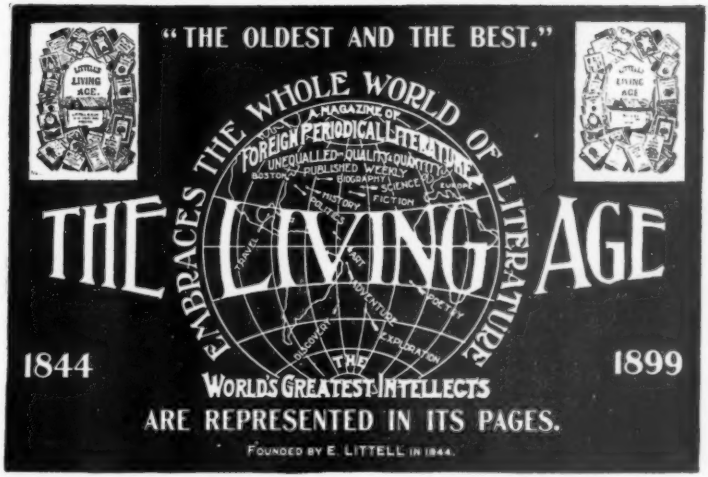
II. Bemerkung über die Spannung des Wasserdampfes bei Temperaturen die dem Eispunkte nahe sind. (1858.)

III. Ueber die Spannung des Dampfes von Mischungen aus Wasser und Schwefelsäure. (1858.)

Nr. 102. Ueber physikalische Kraftlinien. Von James Clerk Maxwell.

Nr. 103. Joseph Louis Lagrange's Zusätze zu Eulers Elementen der Algebra. Unbestimmte Analysis.

2. *University of Tennessee Record of Scientific Engineering.* Published by the University of Tennessee Press, Knoxville, Tennessee.—Number 7 of this publication, for November, 1898, pp. 343–405, has been recently received. It contains a number of original scientific papers, and gives evidence of the scientific activity at the University of Tennessee. Among the papers we notice one on Nutrition Investigations, by Charles E. Wait; several papers on Chemical Analytical Methods; another on Meteorological Observations by means of Kites, by W. M. Fulton; also, Notes on the Flora of West Tennessee, by S. M. Bain.



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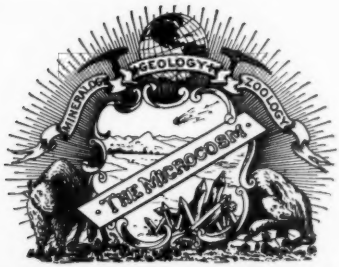

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(1) Described in this Journal Sept., 1895 (2) Ibid Nov., 1887. (3) Proc. Roch. Acad. Sci., Vol. I. (4) This Journal Aug., 1888. (5) Ibid July, 1893. (6) Ibid June, 1894. (7) Ibid Nov., 1892.

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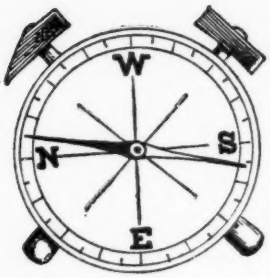

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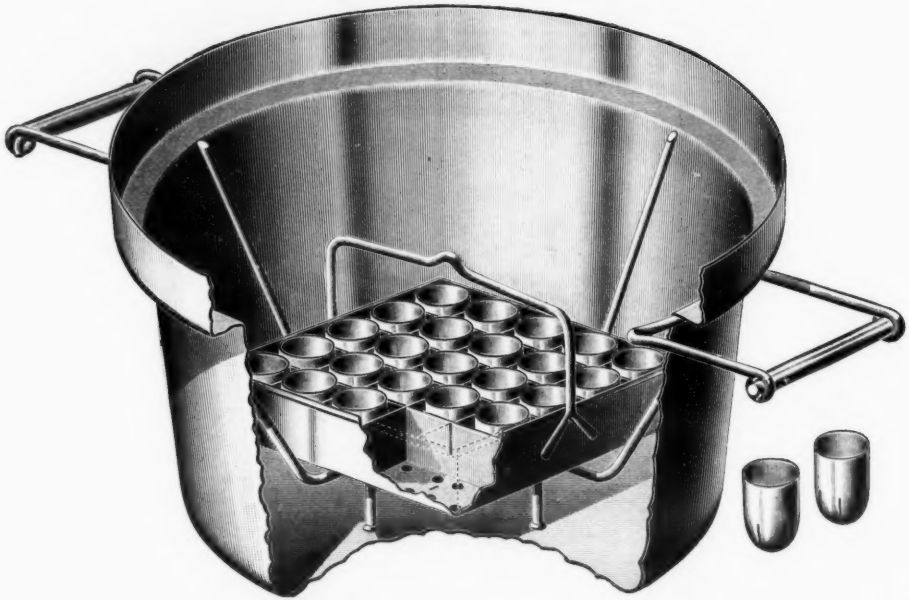

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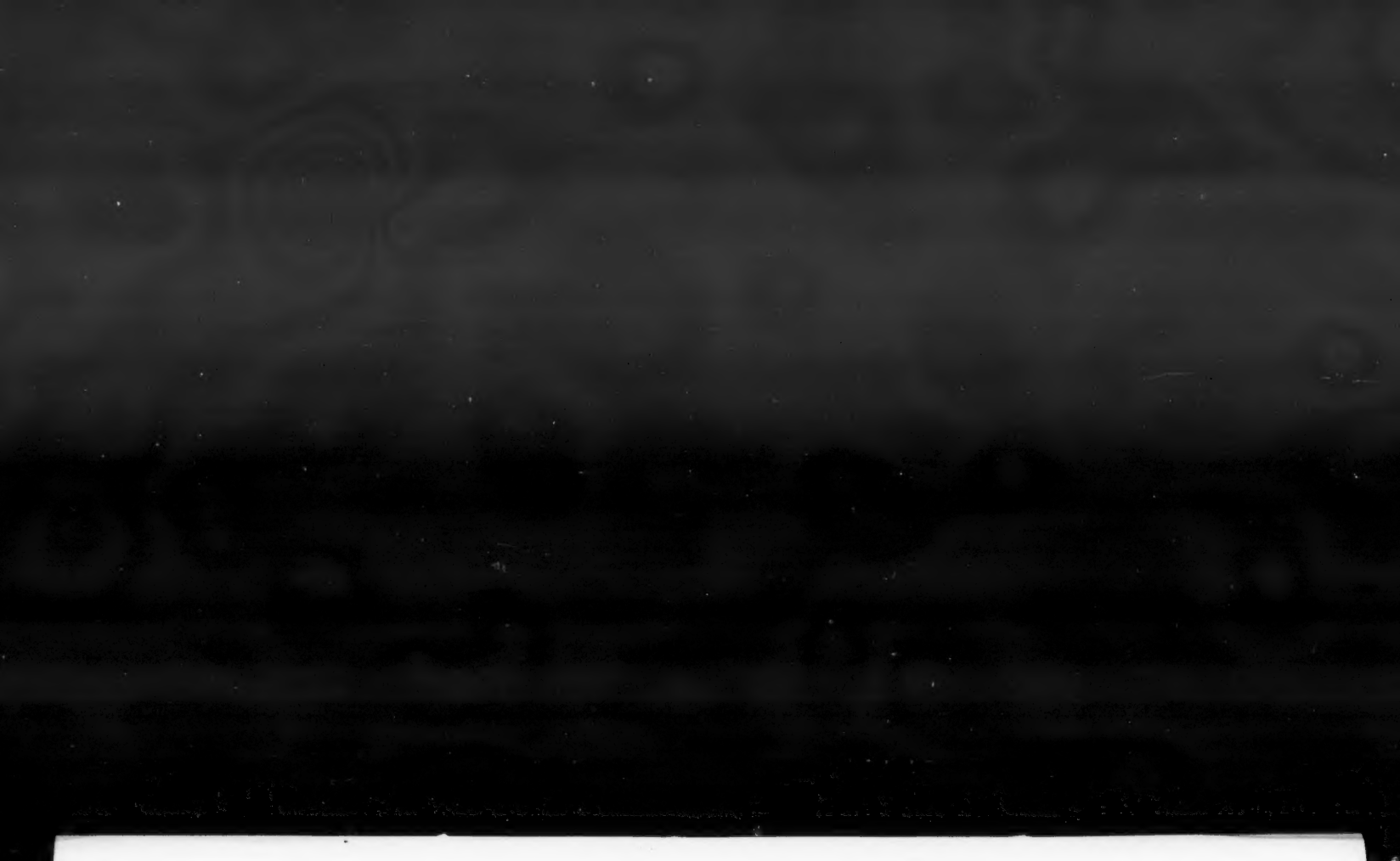
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